Technische Universität Berlin

Fachgebiet
Dynamik und Betrieb technischer Anlagen

Introduction to Wet Sulfuric Acid Plants Optimization Through Exergoeconomics

Master's thesis

Borja Xicoy Almirall

Professor:

Prof. Dr.-Ing. Günter Wozny

Tutor:

Dipl.-Ing. Jan Schöneberger

June 2009

Kurzfassung

Die Diplomarbeit ist eine Einleitung zur thermoökonomische Analyse in Schwefelsäure Anlagen. Eine Referenzanlage mit der folgenden charakteristiken wird analysiert: eine Schwefelbrennkammer zur Oxidation schwefelwasserstoffhaltiger Gase, ein durch Luftzufuhr abgekühlter Naß-Katalyse Prozess und eine Absorptionskolonne zur Produzierung von Schwefelsäure mit 78 Massenprozent H_2SO_4. Außerdem wird Wasserdampf von 40 bar und 5 bar erzeugt.

Die thermoökonomische Analyse besteht aus drei Schritten: Zuerst wird eine Exergieanalyse unter Anwendung der kommerziellen Software CHEMCAD und des Hilfsprogramms CHEMEX durchgeführt. CHEMEX wurde im Rahmen dieser Diplomarbeit entwickelt und dient zur Berechnung der chemischen Exergie von Elektrolytlösungen. Im nächsten Schritt wird eine Wirtschaftlichkeitsanalyse zur der Berechnung der nivellierten Kosten der Anlage mittels PEC und weiteren Kostenschätzungsmethoden durchgeführt. Im dritten Schritt der Analyse werden Exergie- und Wirtschaftlichkeitsanalyse durch die Aufteilung der nivellierten Kosten auf alle Strömen der gesamten Anlage bezüglich ihrer Exergiewerte kombiniert. Dafür ist ein lineares Gleichungssystem mit den Kostbilanzen jeweiliger Analgenkomponente und komponentenspezifischen Hilfsgleichungen zu lösen. Schließlich werden drei kosteneffektive Optimierungsschritte auf die Referenzanlage angewendet, wobei exergoökonomische Kennzahlen die jeweiligen Optimierungsschritte motivieren.

Abstract

This thesis pretends to be an introduction to the use of thermoeconomics in sulfuric acid plants. A reference plant with the followings features is examined: a sulfur burner which oxidizes hydrogen sulfide gases, a wet-catalysis process which is cooled by means of air quenching, and an absorbtion column that produces sulfuric acid of 78 wt.%. Moreover, the plant has two heat-recovery boilers that produce steam at 40 bar and 5 bar.

The thermoeconomic evaluation consists of three steps: In the first step, an exergy analysis is performed by using the commercial software CHEMCAD and the tool CHEMEX, which was designed for this work and takes into account the activity coefficients of water and sulfuric acid in liquid mixtures for the calculation of the chemical exergies; In the second step, an economic evaluation is carried out in order to calculate the plant levelized costs by means of the PEC and cost estimating techniques; In the third step, both exergy and economic analyses are combined by distributing the levelized costs among all plant streams, regarding to its exergy value, in terms of a linear equation system composed of the cost equation of each plant component and some auxiliary equations. Finally, three possible cost-effective optimizations are studied regarding to the reference plant by applying the methods of the thermoeconomic optimization based on thermoeconomic key indicators.

Contents

List of Tables

List of Figures

List of Acronyms

AFUDC Allowance for Funds Used During Construction

BBY Balance at the Beginning of the Year

BD Book Depreciation

BL Book Life

BPV By-Products Value

CC Carrying Charges

CELF Constant-Escalation Levelization Factor

CI Cost Index

CRF Capital Recovery Factor

DC Direct Costs

EPRI Electric Power Research Institute

FC Fuel Costs

FCI Fixed-Capital Investment

HETP Height Equivalent to a Theoretical Plate

IC Indirect Costs

LMTD Logarithmic Mean Temperature Difference

MAR Minimum Acceptable Return

MPQ Main-Product Quantity

MPUC Main-Product Unit Cost

NRTL Non-Random Two Liquid Model

OAM Operating And Maintenance costs

OFSC Off-Site Costs

ONSC On-Site Costs

PEC Purchase Equipment Cost

PFI Plant-Facilities Investment

RCEAF annual Recovery of Common Equity

ROI Return On Investment

SUC Startup Costs

TCI Total Capital Investment

TCR Total Capital Recovery

TDI Total Depreciable Investment

TRR Total Revenue Requirement

WC Working Capital

WSA Wet Sulfuric Acid

Nomenclature and Units

A	m^2	Area
A	euros	Annual amount of money
A	several	Design variable
A_Q	m^2	Cross sectional area; cross section
$\dot{C}$	$\frac{\text{euros}}{\text{h}}$	Cost flow rate
C_P	euros	Component price
D	m	Diameter
$E,\ \dot{E}$	kJ; kW	Exergy; exergy flow rate
$\dot{E}_D$	kW	Exergy destruction flow rate
$\dot{E}_L$	kW	Exergy loss flow rate
F	euros	Future value
F	$Pa^{1/2}$	Load factor
F_{Lang}	$-$	Lang factor
H_a	m	Tower height
I	$-$	Cost index
L	m	Longitude
N	$-$	Number of tower stages
P	$euros$	Present value
$Q,\ \dot{Q}$	kJ; kW	Heat; heat flow rate
R	$\frac{\text{kJ}}{\text{kmol·K}}$	Molar universal gas constant
$S,\ \dot{S}$	$\frac{\text{kJ}}{\text{K}};\ \frac{\text{kW}}{\text{K}}$	Entropy; entropy flow rate
$\dot{S}_{gen}$	kW	Entropy generation flow rate

T	K; °C	Temperature
U, $\dot{U}$	kJ; kW	Internal energy; internal energy flow rate
U	kJ	Heat
V	m^3; L	Volume
$\dot{V}$	$\frac{m^3}{s}$	Volumetric flow rate
W, $\dot{W}$	kJ; kW	Work; power
$\dot{Z}$	$\frac{euros}{h}$	Investment and operating and maintenance costs flow rate
c	$\frac{euros}{kJ}$	Average cost per unit of exergy
e, $\overline{e}$	$\frac{kJ}{kg}$; $\frac{kJ}{kmol}$	Specific exergy
f	−	Exergoeconomic factor
g, $\overline{g}$	$\frac{kJ}{kg}$; $\frac{kJ}{kmol}$	Specific free enthalpy
g^E	$\frac{kJ}{kmol}$	Specific excess molar free enthalpy
h, $\overline{h}$	$\frac{kJ}{kg}$; $\frac{kJ}{kmol}$	Specific enthalpy
i_{eff}	%	Effective interest rate
i_x	%	Type of financing
k	$\frac{W}{m^2 \cdot K}$	Overall heat transfer coefficient
p	Pa; bar	Pressure
p_{oo}	Pa; bar	$x_e p_o$; Partial pressure of the xth-component in the reference environment
m, $\dot{m}$	kg; $\frac{kg}{h}$	Mass; mass flow rate
n, $\dot{n}$	kmol; $\frac{kmol}{h}$	Number of moles; molar flux
r_n	%	Nominal inflation rate

$s,\ \overline{s}$	$\frac{\text{kJ}}{\text{kg}\cdot\text{K}};\ \frac{\text{kJ}}{\text{kmol}\cdot\text{K}}$	Specific entropy
$u,\ \overline{u}$	$\frac{\text{kJ}}{\text{kg}};\ \frac{\text{kJ}}{\text{kmol}}$	Specific internal energy
v_f	$\frac{\text{m}^3}{\text{m}^2\cdot\text{h}}$	Volumetric liquid factor
v_g	$\frac{\text{m}}{\text{s}}$	Gas velocity
x	$-$	Molar fraction
y	$-$	Liquid molar fraction
y_D	$-$	Exergy destruction ratio regarding to the fuel
y_D^*	$-$	Exergy destruction ratio regarding to the total exergy destruction
y_L	$-$	Exergy loss ratio
z	$-$	Gas molar fraction

Greek

α	$-$	Alpha factor
γ	$-$	Activity coefficient
ϵ	$-$	Error
η	$-$	Efficiency
ρ	$\frac{kg}{m^3}$	Density
τ	$hours$	Annual working hours
Φ	$-$	Exergetic efficiency

Superscripts

$*$	Plus expenses due to exergy losses
CH	Chemical
CI	Capital investment
KN	Kinetic
OM	Operating and maintenance costs
PH	Physical
PT	Potential

Subscripts

CV	Control volume
F	Fuel
I	First improvement
II	Second improvement
III	Third improvement
L	Levelized
M	Mixture
P	Product
(a)	Entropy generation method
abs	Absolute
(b)	Exergy balance method
ce	Common equity

cu	Current (euros)
ct	Constant (euros)
d	Debt
e	Dead state
e	Outlet
g	Gas Phase
i	Inlet
j	Flow; year
k	Component
l	Liquid phase
o	Environmental conditions; reference plant
ps	Preferred stock
q	Heat
rel	Relative
sc	Isentropic compressor
w	Work

Chapter 1

Introduction

Sulphuric acid, H_2SO_4, is a colorless, viscous liquid with a normal boiling point of ca. 274 °C. H_2SO_4 is the largest volume chemical commodity produced and it is sold or used commercially in a number of different concentrations: 78% (concentration of work's interest), 93%, 96%, 98-99%, 100% and as various oleums [17].

Sulfuric acid has a number of large-scale uses not only within the chemical industry but in other industries as well. By far the most important user is the phosphate fertilizer industry. Other important applications of sulfuric acid are found in petroleum refining, pigment production, steel finishing, electronic chips, detergents, plastics, and man-made fibers, as its use in batteries. Many specialty areas of the chemical industry also use varying amounts of sulfuric acid including the production of pharmaceuticals and fluorine chemicals [4]. Concentrated sulfuric acid is also a good dehydrating agent and under some circumstances it functions as an oxidizing agent [17]. There is hardly an article of commerce which has not come at one time or another into contact with sulfuric acid during its manufacture or in the manufacture of its components [30].

The consumption of sulfuric acid has many times been cited as an indicator of the general state of a nation's economy, in some books has been mentioned as "a reliable barometer of industrial activity" [30], and although many other indicators (such as energy consumption) might be today regarded as more important, sulfuric acid consumption still follows general economic trends. For example, the recession that resulted from the "energy crisis" of 1974 was clearly reflected in the pattern of sulfuric acid consumption in the following years. The recession a few years later was similarly accompanied by a generally declining trend in sulfuric acid consumption

starting in mid-1980 [4]. Without going any further, the uncertain future of the actual international economic recession may have also a strong influence in the worldwide's sulfuric acid consumption.

As a previously understanding explanation for the next sections, the process of sulfuric acid production consists basically of three steps: At the first step, it is obtained the principal starting material for its production, the sulfur dioxide. SO_2 can be produced by different methods from various raw materials, such as elemental sulfur, spent (contaminated and diluted) sulfuric acid, and hydrogen sulfide; specifically for this work, the raw material will be hydrogen sulfide concentrated gases. At the second step, sulfur dioxide is oxidized to sulfur trioxide. Finally, at the third step, the sulfur trioxide is treated with water and concentrated sulfuric acid in different ways, depending on the type of sulfuric acid production method, to form sulfuric acid. For this reason, it must be clarified that when in the next section several sulfuric acid production processes are explained, such as the chamber process or the contact process, these processes only differ basically in the way SO_2 is chemically treated to become SO_3 and later sulfuric acid, and not in the way SO_2 is obtained, which could be managed by many different processes and consequently, it is not taken into account.

1.1 The Process and its Development

In the late Middle Ages, sulfuric acid was formed in small quantities in glass vessels and was already an important item of commerce. Later, with the introduction of lead chambers by Roebuck in the mid-eighteenth century it was possible to achieve higher production levels. In other words, the effective industrialization of sulfuric acid production was reached. During that century, the nitrogen oxide process was the process used to produce sulfuric acid and physicists as Gay-Lussac and Glover were important for its development, introducing nitrogen oxides recovery methods which improve the process. However, at the beginning of the nineteenth century, Phillips, in Bristol, England, patented the oxidation of sulfur dioxide to sulfur trioxide over a platinum catalyst at high temperature, which later led the development of the today's most used acid sulfuric production technology: the *contact process*.

The growth in popularity of the contact process stimulated new competitive ef-

forts to improve the lead chambers process, such as the significant replacement of the lead chambers with acid-irrigated towers. However, the development of relatively cheap vanadium catalysts and the increasing demand for concentrated sulfuric acid brought the international sulfuric acid production by nitrogen oxide plants into a steady declension. This fact became worse, taking into account that the product concentration in nitrogen oxide processes is limited to a maximum of 70-75%, while the contact process is capable of producing concentrated (98%). By 1960, these plants had shrunk its production to ca. 15% in Western Europe and North America. These days, all sulfuric acid is manufactured by the contact process. Some plants have a sulfur dioxide conversion efficiency exceeding 99.8%. The basic principle of the process remains the same today as when it was first introduced in the 1930s. Anyhow, the nitrogen oxide process has continued to be an object of interest, especially for the processing of gases with extremely low SO_2 content (0.5-3 vol%) [4].

Following the explanation of the contact process's evolution, at the beginning of the twentieth century, BASF patented a vanadium pentoxide catalyst, which succeeded in replacing the Phillip's platinum catalyst because of its robustness to catalyst poisons and its considerably lower cost. In terms of work's interest, the wet contact process was developed by Lurgi using a vanadium catalyst for converting moist sulfur dioxide-containing gases. This process is known as "wet", since the air used to obtain sulfur dioxide is not dried, so an amount of water is produced during the combustion of the raw material. This fact allows the process for reducing capital and operating expenses in terms of drying machinery, heat recovery, lower consumption of cooling water and by-product production.

In the succeeding years, a number of factors such as the rise in the consumption of sulfuric acid and the progressively use of sulfur dioxide containing-gasses with higher sulfur concentrations as a raw material basis of the industry, introduced improvements in the contact process technology. The double absorption contact process or also known as the double-catalysis process, patented in 1960 by Bayer, is a significant example of this further development. Higher SO_2 conversions and also a reduction of the SO_2 emissions are fulfilled by adding a preliminary SO_3 absorption step ahead of the final catalytic stages. In fact, some environmental regulations from principal industrial countries made the use of the double-absorption process

mandatory in new plants [17, 4]. In this work, a conventional contact process plant, concretely using a wet-catalysis process, is examined.

1.2 An Introduction to Contact Processes

Generally, in contact processes, a gas mixture containing sulfur dioxide is passed together with oxygen over a catalyst to oxidize the sulfur dioxide to sulfur trioxide. The sulfur trioxide is then absorbed in sulfuric acid where it reacts with added water to form more sulfuric acid. So, in general terms, the process could be separated in two main steps:

- Step 1. Catalytic conversion of sulfur dioxide to sulfur trioxide
- Step 2. Absorption of sulfur trioxide

In addition, two more steps have to be considered: the gas drying step, and the acid cooling step. The first will not be studied, since our plant of study works under a wet-catalysis process and as said before, these plants operate without air drying. The cooling step will be discussed in next sections. Figure 1.1 shows a diagram of the standard contact process.

1.2.1 Catalytic Oxidation of Sulfur Dioxide

The converter, a reactor in which sulfur dioxide is oxidized catalytically to sulfur trioxide, plays a significant role in the plant since the rest of the process is strongly affected by the efficiency of its SO_2-SO_3 conversion.

$$SO_2 + 0.5O_2 \leftrightarrow SO_3 \tag{1.1}$$

The reaction is highly exothermic and generally it is carried out under adiabatic conditions, so the temperature of the solid catalyst bed rises. The SO_2-SO_3 equilibrium becomes increasingly unfavorable for SO_3 formation as temperature increases up to 410-430 °C. Unfortunately, this is about the minimum temperature level required for typical commercial catalysts to function. Consequently, to achieve a high final SO_2 conversion, the total catalyst mass is divided up into several catalyst beds, and the hot gas leaving each bed is cooled to the minimum working temperature of the catalyst before it enters the next bed. For a normal contact process without

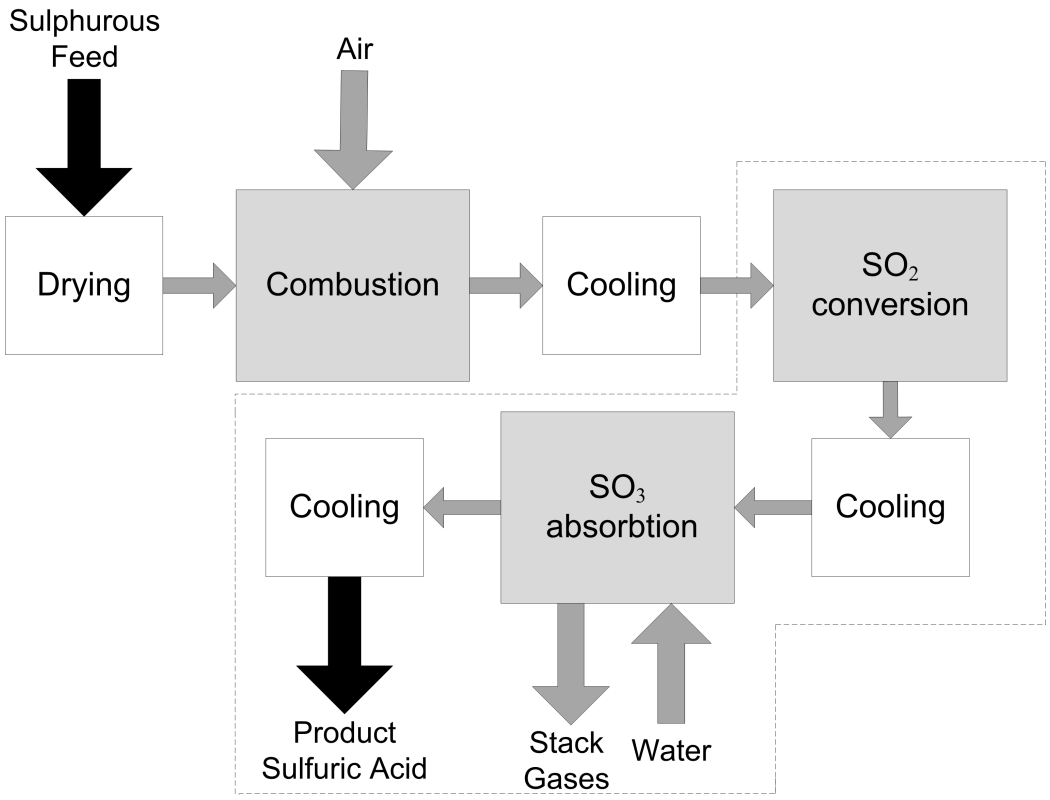


Figure 1.1: Contact process diagram. The SO_2 conversion step is internally cooled (between beds).

intermediate absorption (single absorption), the maximum achievable SO_2 conversion with a typical four-bed converter is ca. 98%. This contrasts with a final SO_2 conversion >99.5% in a double-absorption process with the same number of catalyst beds. Figure 1.2 shows the reaction profile for both a single-absorption and a double-absorption processes (feed gas: 8.5 vol% SO_2), together with the SO_2 conversion attainable in each bed. The conversion operates under adiabatic conditions and both converters contain 4 beds.

In terms of converter design, the choice of an accurate converter for user needs depends on a large number of interacting parameters. The most important are the sulfur dioxide concentration, the gas-flow rate, the number of beds, the specific catalyst quantity and its distribution between the individual beds, the pressure drop, so as the gas-inlet temperatures and pressures at the individual beds. Normally, the converter is designed as a vertical cylindrical vessel, with the catalyst beds mounted above one another in separate compartments; the catalyst bed height may vary from 200 mm to 1000 mm; and the specific catalyst quantity required for production

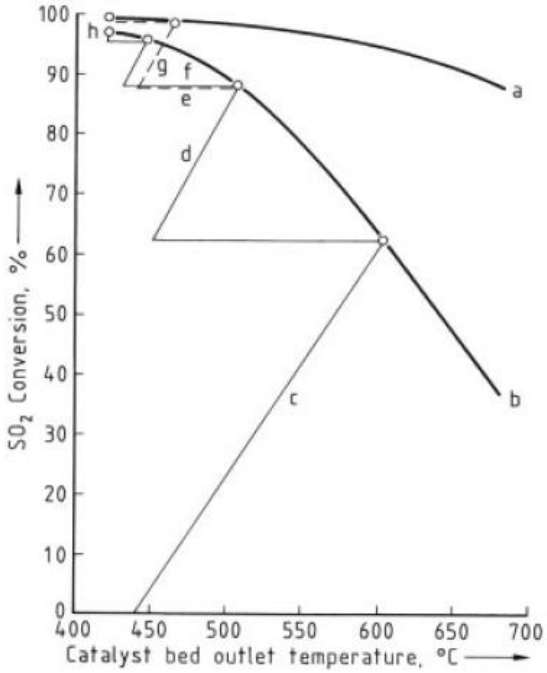


Figure 1.2: Comparison of reaction profiles. a) Double-absorption process equilibrium curve after intermediate absorption; b) Equilibrium curve for normal contact process; c), d), g), h) Adiabatic reactions in beds 1, 2, 3, and 4; e) Cooling and intermediate absorption; f) Cooling [4]

of 1 t/d of sulfuric acid is ca. 200-260 L for a single-absorption plant [4]. The optimum method of cooling the reaction gas between catalyst beds is a function of the composition and initial temperature of the feed gas, parameters that have to be assumed in order of choosing an adequate heat exchanger. Its constructive material and range of operating temperatures depend on these parameters, as discussed in Section 1.2.3.

1.2.2 Absorption of Sulfur Trioxide

Sulfur trioxide gasses, formed by the catalytic oxidation of sulfur dioxide, pass from the bottom to the top through the absorber, which is uniformly irrigated from the top with liquid-phase sulfuric acid. The H_2SO_4 liquid stream absorbs the SO_3 gasses and it reacts with existing or added water to form more sulfuric acid with a desired concentration. In our case, it is added as much water as to form 78 wt% sulfuric acid at the absorber liquid outlet.

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{1.2}$$

Since at lower acid concentrations the water vapor partial pressure is higher, there is a correspondingly greater risk that sulfuric acid mist will form as a result of direct reaction of sulfur trioxide in the gas phase with water vapor above the acid.

Process gas leaving the converter system is cooled by a gas-gas heat exchanger or a steam generator, preferably in conjunction with a feed-water preheater, to a temperature of 180-220 °C before entering the absorber [4]. It is essential that the wall temperature in the gas coolers never drops below the acid dewpoint (110-160 °C, depending on the gas composition [4]); otherwise there is an acute danger of corrosion due to condensing acid, as well as mist formation. Gas entering the absorber is therefore not completely cold, and it releases heat to the absorber acid as it passes through the absorber.

A substantial amount of heat is also generated in the absorber acid from absorption of sulfur trioxide and the formation of sulfuric acid. Consequently, the acid temperature rises by an extent that depends on the acid-circulation rate. Efficient sulfur trioxide absorption depends not only on uniform acid and gas distribution in the absorber but also on ensuring that the temperature and concentration of the absorber acid remain at the optimum values. The acid concentration is held constant by adding process water or dryer acid to acid leaving the absorber. The optimum acid-inlet temperature depends on design conditions, between 60-80 °C in most plants, maintained at that level by indirect cooling [4]. The attainable SO_3 absorption efficiency is generally >99.9% [4].

Despite efficient gas drying and optimum conditions for sulfur trioxide absorption, it is often impossible to prevent mist formation completely. Such mists are undesired because of both corrosion in the process and stack emissions. In order to decrease them, there are various designs for mist eliminators, and not all operate on the same principle. Nevertheless, in this thesis, mist eliminators are not taken into account, but it might be of interest in further studies.

1.2.3 Constructive Elements

There are many different types of sulfuric acid production processes, depending on the sulfur source (elemental sulfur, waste acid, SO_2, H_2S, etc.), the type of absorbtion (single or double), the way the gas water is treated (dry or wet processes), and so forth. In this subsection, based in bibliography [4, 17, 31], constructive

characteristics of the main equipment that takes place in an elemental wet process are discussed. This equipment consists of *pumps, compressors, burners, acid cooling, steam production equipment, contact hordes*, and *absorbtion columns.*

Pumps

The standard type of pumps for sulfuric acid plants are the one-stage *centrifugal pumps*, powered by an electric motor. Although, *horizontal pumps* can be used, the most common nowadays are the *vertical submersible pumps* (Figure 1.3) [31]. The reasons are: the use of electric motors with a soft start, which save in armature and piping; leak reduction; and easy installation. In the case of horizontal pumps, the most used are the *horizontal magnetic pumps* due to its proper leakage reduction. *Membrane pumps* and *canned motor pumps* are especially used for liquid-phase SO_2 and SO_3 circulation.

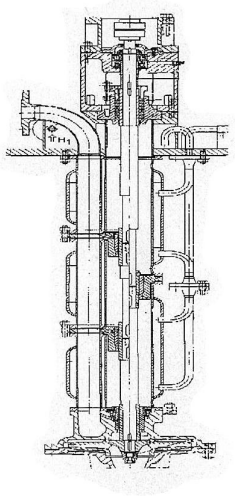


Figure 1.3: Vertical submersible pump [31]

Compressors

The function of compressors is the flow of dried SO_2-containing gasses and dried air through the entire plant, and the overcome of flow resistances in equipment and piping. Almost exclusively, it is used *centrifugal compressors* (Figure 1.4), with a power performance up to $300000\,\mathrm{Nm^3h^{-1}}$ (gas at $50\,^{\circ}\mathrm{C}$) increasing the pressure by 1 bar [31]. The actuators can be either *fixed-speed* or *variable-speed* electric motors (medium frequency or *cascade control*). In terms of energy saving, flow resistances

in equipment and piping should be optimized, as well as the use of high efficiency machinery.

Fixed-speed compressors can operate in a load range between 70 and 105%. In spite of lowering the compressor efficiency, in terms of load range, the easiest regulation method is by means of a valve. Another improving option is by using an *inlet vane control* which led to higher efficiencies with a load range between 50 and 105%. The power limitations of a compressor lie on the peripheral speed and the impeller type of material. The impellers are fabricated as welded assemblies, while the housing either with cast iron or as weldment. The sealing used in the shaft of the compressor's body are *labyrinth seals* and in the case of SO_2 containing-gasses, additionally, *air purge fittings*.

Centrifugal compressors are finished with *contact bearings*, having an electric motor rotation speed between 4000 and 9000 rpm. The connections between the compressor and its internal parts, as with plant piping, are fulfilled with *flange connections*, which are sealed against SO_2- and low concentrated H_2SO_4-containing gasses.

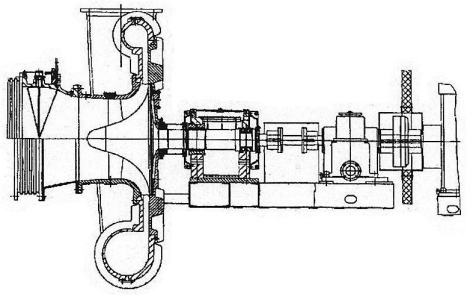


Figure 1.4: Centrifugal compressor [31]

Burners

The burners, also known as incinerators, perform the combustion of sulfur-containing gasses in order to produce sulfur dioxide. Current practice is to use *horizontal brick-lined combustion chambers* with dried air and atomized sulfur gas introduced at one end. Atomization usually is performed either by *spray nozzles* or by mechanically *driven spinning cups*. Sulfur burners operate normally at moderate pressures in the range of 135.8-170.3 kPa, using air supplied by the main blower for the plant. It

must be taken into account that at high flame temperatures (approximately from 1200 °C on), nitrogen can react with oxygen to form nitrogen oxides, NO_x.

The temperature of gas leaving the sulfur furnace is a good indication of SO_2 concentration. By burning pure sulfur, at a combustion air temperature of 55 °C corresponds to ∼10.0 vol% SO_2, 1034 °C-11.0 vol% SO_2, 1112 °C-12.0 vol% SO_2 [17]. Other temperatures and concentrations are in similar proportion.

In the case of H_2S burning, special types of spray nozzles are required because of its highly exothermic combustion.

Converters. Catalyst Beds

The principal installation in a sulfuric acid production plant is the converter, with its corresponding catalyst beds. On the catalyst bed, the sulfuric dioxide reacts with oxygen yielding sulfur trioxide.

Normally, the converter is designed as a vertical cylindrical vessel, with the catalyst beds mounted above one another in separate compartments. It is usually used *adiabatic beds*; that is, the bed is not inside cooled, so the heat of reaction is absorbed by the flowing gas. Although, an *isotherm reactor* would be more efficient, in terms of SO_2 conversion, it is not feasible yet [4].

In a fixed bed reactor, the gas flows from the top to the bottom of the catalyst bed. The main reason is because of the flow resistance by gas holding solids, which moreover can crumble the body of the catalyst. The catalyst mass is supported by a metallic bed grate, which consists of a base layer of ceramic packing. This prevents direct contact between the catalyst and the grate, in order to avoid corrosion. The catalyst bed is itself covered with another layer of packing. This ensures uniform gas and temperature distribution over the surface of the catalyst (Figure 1.5), at the same time that prevents the catalyst from leaving cavities in the bed. The bigger the converter diameter is, the more difficult the gas distribution is performed.

In a sulfuric acid plant, three types of converters are usually used: *brick-lined, steel,* and *stainless steel* (see Figure 1.6).

The *brick-lined converter* consists of a cylindrical steel jacket (C-steel), which internally is completely lined with acid-proof bricks. The compartments separators are self-supporting domed structures made of shaped bricks, which require brick columns to support the catalyst-bed grates. This type of converter represents a

Figure 1.5: Catalysts O4-115 SR 10x5 [24]

conservative design guaranteeing long lifetime together with a high thermal inertia. This makes easier to operate with fluctuating gas loads and start-up after idle periods. However, they are rarely used according to the following reasons: the domes' diameter is limited up to 12 m, which limits at the same time the converter diameter; the high costs of the brick-construction; the not 100% gas-tightness, which lead to lower SO_2-conversions; the elevated weight of the equipment and its corresponding foundation; and difficult and expensive reparations.

The *steel converter* (C-steel) is an answer to the the brick-lined converter problems. Flat steel plates are used as compartment separators, instead of domed structures, which are gas-tight thanks to a steel jacket, usually welded to a supporting central pipe. Depending on the working temperature, the separations of the bed1/bed2 and bed2/bed3 are isolated. This type of converters are mostly used in lands where stainless steel is an expensive import article [31]. However, steel converters are more economical compared with a stainless-steel converter and are appropriate for treatment of gases with lower SO_2 loads [4]. The *stainless-steel converter* is nowadays the standard converter in sulfuric acid plants. It is similar to the steel converter, since it consists also on a shell, the tray separators, and the trays, as well as the use of a central supporting tube. The main difference is that these converters are fabricated entirely of stainless or heat-resistant steel allowing a maximal working temperature up to 700 °C and the inertness against catalyst components [31].

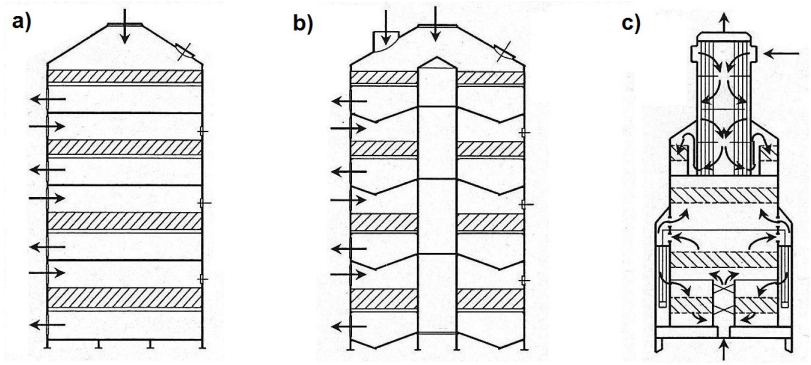


Figure 1.6: Converters: a) brick-lined b) steel c) stainless-steel with integrated heat exchangers (Lurgi) [4]

Absorbers

The standard type of absorbers are *package towers* (Figure 1.7), operating in countercurrent. It consists of a cylindrical vessel, a cover, and a bottom, made of stainless steel and without being brick-lined. This is an advantage when the towers must be replaced during maintenance shut-downs. The absence of a brick lining also implies that a new tower can be completely prefabricated and set onto the existing foundations within a very short period of time. The tower is comprised of three parts:

In the lowest part, it is found the *acid sump*. That is, a liquid pool where the sulfuric acid produced by the absorber is kept. Over the acid level, it is located the gas-inlet: a steel jacket which is welded to the absorber vessel.

In the middle, it is found a dome-shaped grate (60% of flowing cross-section [31]) which supports the packing bed and it is made of acid-proof ceramic material. Through this bed, the irrigated sulfuric acid flows to the bottom of the absorber, while the gas, coming from the lowest part, flows to the top. It is essential to ensure that gas and acid distributions are uniform over the entire tower cross-section, and that the acid flow rate is sufficiently high to wet the entire packing layer completely. Depending on gas conditions, the packing layer may have a height of 4-6 m [4]. At the present time, gas velocities through the bed are between 1.2-1.6 m/s, while irrigated acid densities are between 20-30 $m^3m^{-2}h^{-1}$ [31]. The packing can be either a *structured packing* or a filling composed by small objects made of ceramic materials, such as Novalox and Intalox. These objects have an specific surface in order to

achieve an intensive contact between acid and gas. Structured packing leads to higher absorbtion efficiencies because of a higher surface density, but they are seldom used due to its elevated prices.

At the top of the absorber, there is the stack gasses outlet and the liquid-phase acid inlet with its corresponding irrigation system. Irrigation systems are usually made of cast iron or of stainless steel SX, 1.4575 or 1.4571 [31]. In the top-outlet, a *wire-mesh* or *cartridge filter* is used by means of separating sulfuric acid drops from the stack gasses, as well as acid fog.

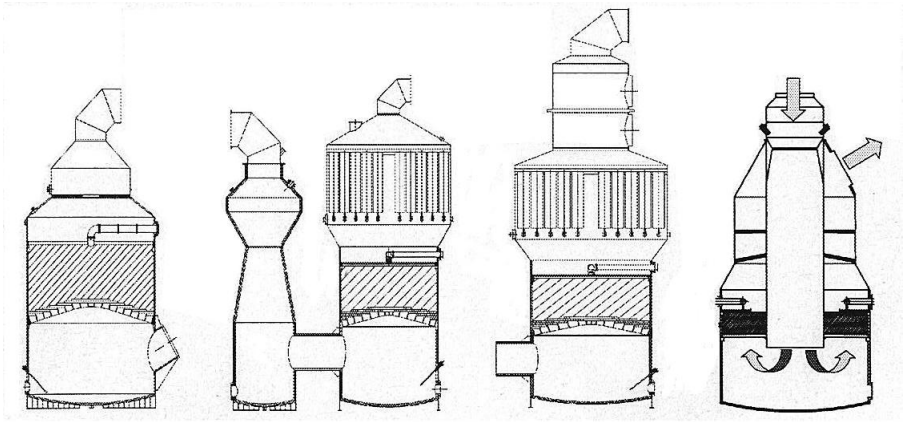


Figure 1.7: Packing-tower absorber with venturi scrubber [31]

Acid Cooling

In determining the efficiency and operating safety of an entire sulfuric acid plant, acid cooling plays a vital role. About 1980, with the introduction of special stainless steels, the field of sulfuric acid cooling experimented an important development. In modern plants, acid cooling is basically composed of three types of coolers:

1. Shell-and-tube coolers
2. Plate-type coolers
3. Air coolers

Intermediate water circuits are also being installed for heat recovery purposes, such as the generation of steam from heat released in the absorbtion system.

Shell-and-tube (s+t) coolers offer many advantages: ease of installation, compact design, and good heat transfer coefficients of 800-1400 $\mathrm{Wm^{-2}K^{-1}}$, depending on the

design conditions and the mode of construction. At present, there are two types of s+t coolers:

1. Coolers fabricated from "standard" stainless steels (1.4571 or 1.4541) and with an additional anodic protection system (on the water, acid or both sites). When both anodic protection on the acid site and a water boiler are used, temperatures up to 130 °C can be endured.
2. Coolers fabricated from special stainless steels (Sandvik SX, 1.4575, etc.), which do not require anodic protection. Maximum temperatures of 120 °C or higher can be endured.

These coolers cover the complete range of operating parameters normally encountered in an absorption system. Sea water, brackish water, cooling-tower water, and closed-loop water can all be used as the cooling medium.

Plate coolers have been increasingly used for sulfuric acid cooling duty. It consists of a package of rectangular plates, which are stacked one across each other and a plate for acid and a plate for water alternatively arranged. Incoming and departing acid and cold water streams flow through the corners of each plate. The sealing materials used today are elastomers such as Viton [4], which can handle acid at temperatures up to a maximum of 110 °C. The advantages of plate heat exchangers are: extremely compact design, good accessibility, easy maintenance and cleaning, and a long lifetime. They can be built with very thin walls, since they have a very high heat transfer coefficient (1850-2300 $\mathrm{Wm^{-2}K^{-1}}$), so it is needed a low specific material requirement for the heat exchange area. Hastelloy C276 has proved to be very satisfactory in plate heat exchangers for sulfuric acid cooling. Maximal temperatures of 90 °C can be reached.

Air coolers are used when the consumption of cooling water is restricted, due to non-availability quantities or expensive costs. In this type of coolers, the acid flows through stainless steel tubes arranged horizontally in flat bundles, equipped with external fins to improve heat exchange. The cooling air is forced past the tubes by a fan, so the heat transfer coefficient is between 30-40 $\mathrm{Wm^{-2}K^{-1}}$. The acid temperature is limited to 80 °C. In the case of having anodic protection, higher temperatures can be hold. Air coolers are relatively expensive to install, and a considerable amount of power is also required to drive the fans. However, it is

compensated by saving water and its long lifetime of 30 years, due to the use of stainless steel.

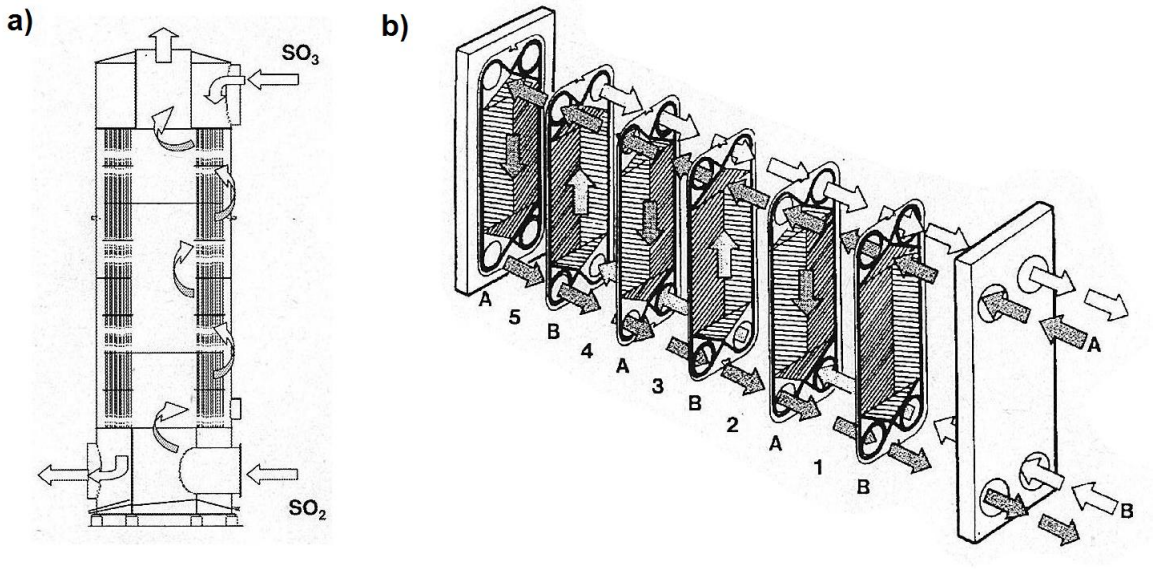


Figure 1.8: Heat exchangers: a) Gas/gas b) Plates [31]

Steam Production Equipment

The reactions in sulfuric acid production processes are exothermic, so reaction heat can be used to generate vapor steam. In this thesis, the following equipment is discussed: *economizer, heat-recovery boiler*, and *superheater*. In a steam production recovery-system, first, the water is heated near the vapor saturation point in the economizer; then, the saturated water flows to the heat-recovery boiler, where it is totally evaporated; finally, the saturated vapor is super heated in the superheater (See Figure 1.10).

An *economizer* consists of a heat exchanger of the type shell-and-tube, which has the function of heating water up to the vapor saturation temperature. This equipment can be installed in the contact group of the plant (converter and catalysts beds). In sulfur-burning plants, hot gas coming from the last catalyst bed at ca. 390 °C to the absorber can be cooled by an economizer down to 170 °C.

The *heat-recovery boiler* is basically a device to produce saturated vapor from hot flue gasses. There are two types: the *water-tube boiler* and the *fire-tube boiler*. In the first boiler, water and vapor flow through the tubes, while the hot gas flows

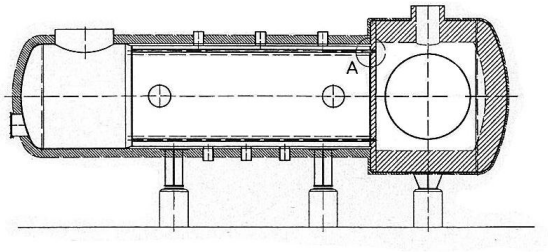


Figure 1.9: Fire-tube boiler [31]

past the tube bundle. Heat exchange can be fulfilled by *natural* or *forced circulation.* In the second type of boiler (Figure 1.9), the hot gas flows through the pipes and the circulation can only be natural. This type of boiler is used in sulphur burning plants. For gas cooling between catalyst beds, an evaporator can also be used when it is working in parallel with a vapor drum situated next to the sulfur burner (Figure 1.10). In that case, the evaporator has to be a fire-tube boiler.

While metallurgical plants operate at constant power and the boiler outlet temperature is allowed for varying between 350 and 400 °C, boiler outlet temperature in sulfur burning plants should be independent of the power and set to 420 °C [31]. For being capable of regulating this temperature, a gas valve has to be used.

Superheaters have the function of heating saturated vapor coming from the boiler to a desired temperature, due to consumer specifications or to be expanded in a turbine. It is composed of a cylindrical vessel and a tube bundle, through which the vapor flows. In sulfuric acid plants based on sulfur burning or high concentrated metallurgical gasses, superheaters are located between the first and the second catalyst beds (Figure 1.10).

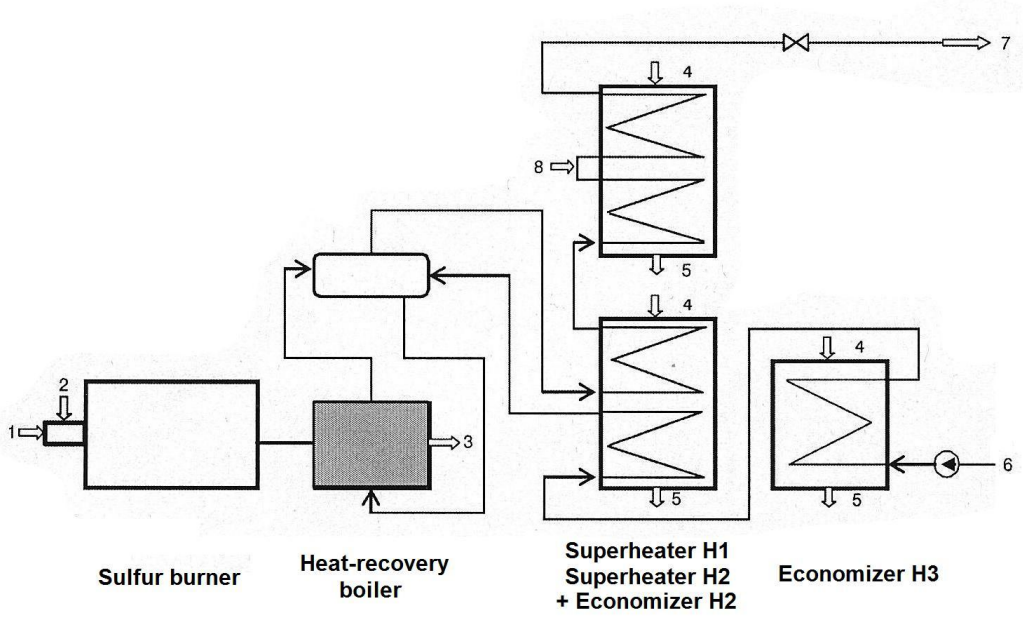


Figure 1.10: Steam production system of a sulfur-burning plant. 1 Sulfur-containing gases, 2 Air, 3 SO_2 rich gas, 4 SO_2/SO_3-inlet, 5 SO_2/SO_3-outlet, 6 feed-water, 7 High pressure-steam, 8 Spray attemperation [31]

Chapter 2

Case Study Process

2.1 An Introduction to Wet-Catalysis Processes

Wet-catalysis processes differ from other contact sulfuric acid processes in that the feed gas still contains moisture when it comes into contact with the catalyst. Generally, sulfur trioxide formed by catalytic oxidation of the sulfur dioxide reacts instantly with the moisture to produce sulfuric acid in the vapor phase to an extent determined by the temperature. The liquid is subsequently formed by condensation of the H_2SO_4 vapor. Nevertheless, in some cases sulfur trioxide is cooled and directly introduced in an absorbtion tower to form sulfuric acid, as in standard contact processes. In summary, as Figure 2.5 shows, it could be said that there are two types of possible wet-catalysis processes: with final sulfuric acid condensation; and with final SO_3 absorbtion. This last type of wet-catalysis absorption processes are of interest to our case study process and will be discussed in next section.

The wet-catalysis process is especially suitable for processing the wet, dust-free gases obtained in the combustion of hydrogen sulfide-containing off-gases, which need to be cooled only to the converter inlet temperature of ca. 440 °C. This fact allows the plant to operate without drying tower reducing plant costs, since the converter can oxidize SO_2 to SO_3 in presence of water vapor. Processing these moisture-laden gases in a conventional cold-gas plant would need cooling to an economically unacceptable extent in order to remove the large excess of moisture. This is an expedient that would only be justified for a gas with a high dust content and a relatively high sulfur dioxide concentration. In this way, wet-catalytic oxidation is being more commonly used for treating weak sulfurous gas streams. The difficulties

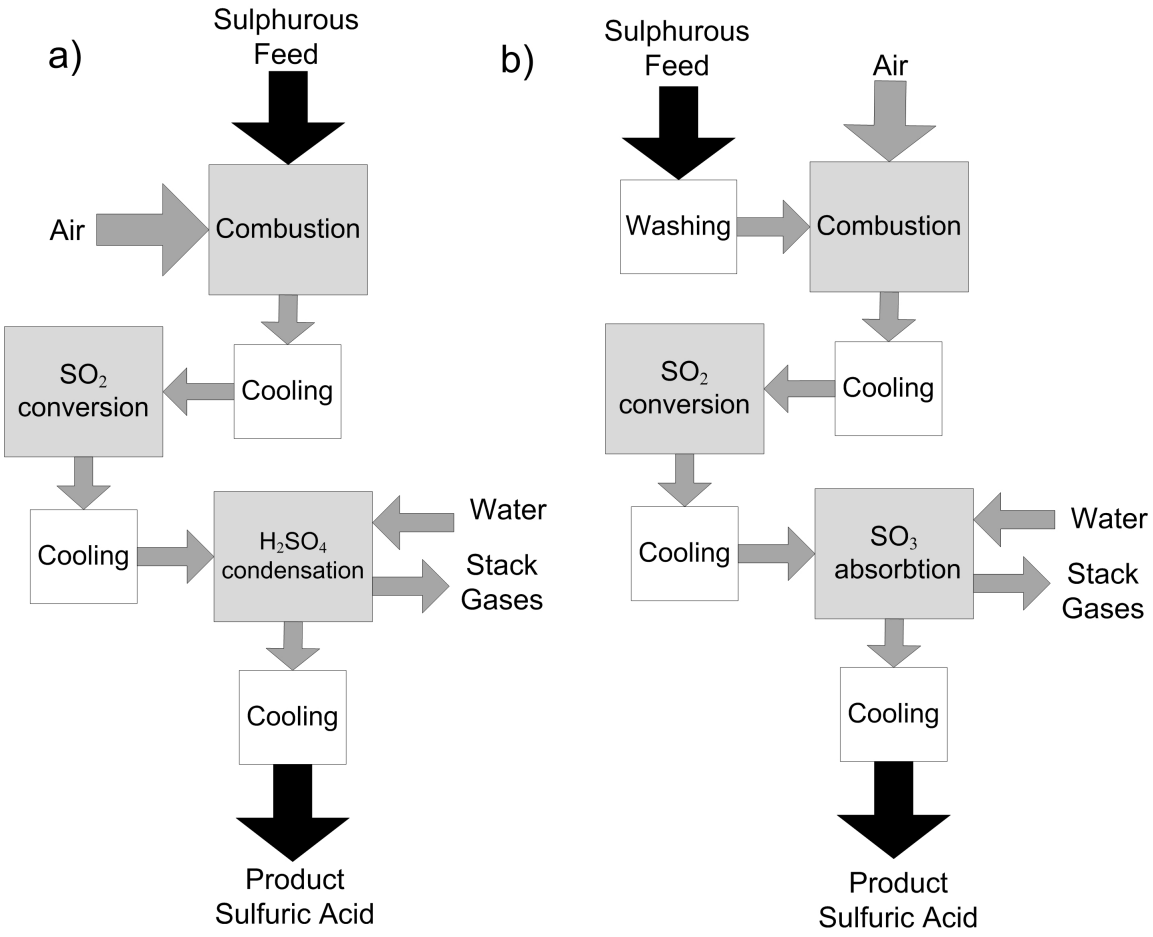


Figure 2.1: Wet-catalysis processes: a) by condensation b) by absorbtion. Wet-catalysis processes by condensation make possible higher product acid concentrations (Topsoe [14])

engendered in this process by the fact that a considerable portion of the sulfuric acid produced occurs in the form of sulfuric acid fogs or mists can be overcome by suitable control of the process and electrostatic demisting (demisting by mechanical means using porous filters).

One disadvantage of the wet-catalytic process is that generally, it is not possible to produce highly concentrated sulfuric acid of the usual commercial concentration of 98 wt% or oleum. As in burning H_2S, SO_2 and H_2O are produced in equimolar proportions, it would seem theoretically possible to produce 100% sulfuric acid directly from the combustion gases. However, as in practice the H_2S containing gases as well as the air for its combustion and the air for converting the SO_2 to SO_3 always contain vapor, the resulting gas always contains more water vapor than corresponds to the proportion H_2O:SO_2=1:1, so that a sulfuric acid of only a mass concentration

of about 80 to 90% is obtained. For this reason, it has been customary to add further water to the process so that a sulfuric acid of a concentration of about 78% H_2SO_4 is obtained. Regardless of this fact, at present, condensation wet processes such as the Haldor Topse Wet Sulfuric Acid (WSA) (Figure 2.2) [26, 15, 14], and Concat (Lurgi) processes are capable for producing 98 wt% sulfuric acid. Absorbtion wet processes can only reach a maximal acid concentration of 93-94 wt% because of the higher moisture content of the gas stream, though.

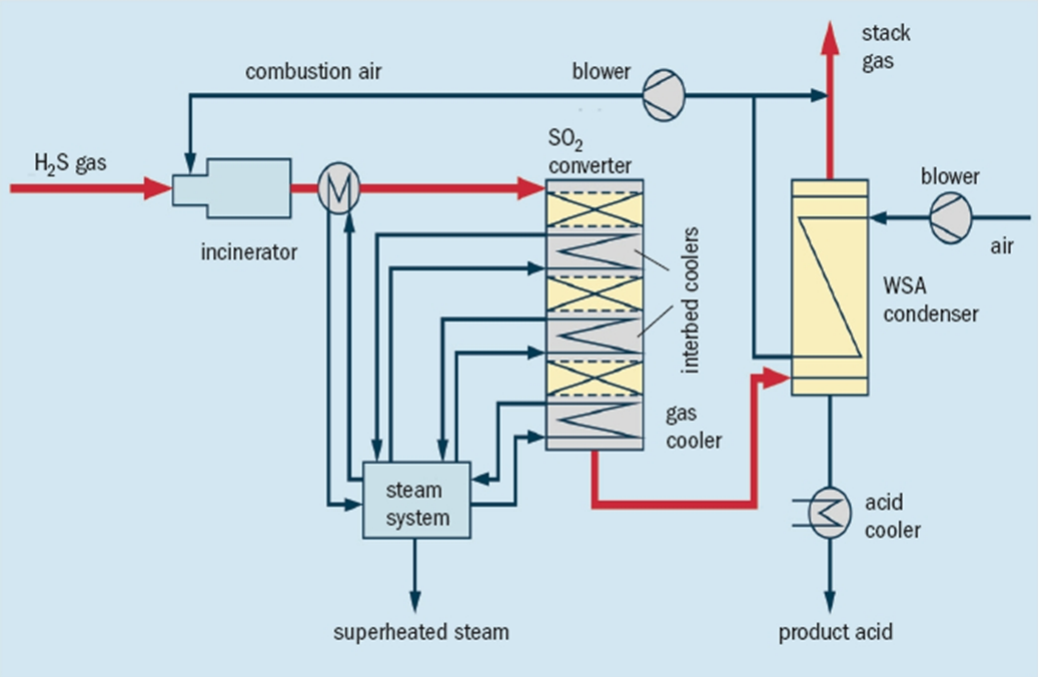


Figure 2.2: Haldor Topse WSA process for H_2S gas [14]

2.2 Reference on Considered Process

The case study process (Figure 2.5) consists on a sulfuric acid production plant of the wet-catalysis type b), as it is shown in Figure 2.1; so, the sulfuric acid is formed by absorbtion of SO_3. The process could be divided into three main stages: *combustion*, *catalysation*, and *absorbtion*. At the first stage, hydrogen sulfide-containing gases are burned with atmospheric air to produce hot SO_2-containing gases, which then are cooled in a waste-heat boiler producing high-pressure steam. At the second stage, the cooled SO_2 enters into a 3-bed catalytic converter to produce SO_3; between each bed the hot gas stream is cooled with air quench. At the final stage, the SO_3-

containing gases are cooled by another waste-heat boiler and subsequently the SO_3 is absorbed in an absorbtion tower by irrigated sulfuric acid to produce the product acid. The stack gases are directly released to the atmosphere. At this stage, external water is required to regulate the sulfuric acid product concentration. The process has been simulated using the commercial software CHEMCAD.

Dust free hydrogen sulfide-containing gases (*stream 1*, 1200 kg/h), coming from an H_2S-washer, enter the process at 30 °C, a pressure of 1.2 bar and a vapor fraction of 0.972 to be burned with atmospheric air in an adiabatic combustion chamber. For the simulation, the combustion chamber is modeled as an equilibrium reactor treating SO_3 and H_2SO_4 as inerts. The air (*stream 17*, 16886 kg/h) enters the process without saturated water, at 30 °C and at the atmospheric pressure of 1.013 bar; with sufficient excess to be used later in the converter and in the quench. Also, the total amount of air mass is exactly selected in such a way that there is not waste air released to the atmosphere, so electrical energy in the compressor can be saved. As the air pressure differs from the H_2S gases pressure, an adiabatic compressor is used to increase it up to 1.2 bar. The air stream mass (*stream 19*, 10444 kg/h) used in the combustion is selected in such a way that the outlet SO_2 gas temperature from the chamber is 1200 °C, in order to avoid the formation of NO_x. The hot, wet, sulfur dioxide-containing gas (*stream 2*, 11644 kg/h) is cooled then to 400 °C in a waste-heat boiler and passed directly to the converter, so the water (*stream 25*, 4680 kg/h) enters the boiler at 100 °C and 40 bar, and it is released as vapor at 250 °C (*stream 26*).

As it was explained in Section 1.2.1, to achieve an optimal catalytic conversion, the inlet converter temperatures have to be fixed and controlled. In this way, the temperatures of the next two converter beds are controlled by the not used atmospheric air in the combustion of H_2S (*stream 20*, 6442 kg/h); these temperatures are of 400 °C and 380 °C, respectively. After each contact horde, the acid stream suffers pressure losses, which depend on the size of the converter. These losses could be small enough, so the acid could condense in next stages of the process. In order to avoid this, the hordes are designed with a length of 0.4 m, the first one, and 10 m and 1 m, second and third horde respectively. The conversion grades SO_2/SO_3 from the first to the third bed are: 89%, 94% and 54%; so the overall conversion is 99.9%. That contrasts with the typical overall conversion in a single absorbtion

process (Section 1.2.1), which is lower than the 99.9% obtained in the reference case. The reason is that in this thesis, the reactions inside the reactors are approached by mathematical methods so the results differ from reality. Additionally, the setup of the reactors is not optimal, but only a reference case.

After the third converter, the SO_3 gases (*stream 8*, 18086 kg/h) are cooled in another waste-heat boiler down to 120 °C, so the water (*stream 27*, 2134 kg/h) enters the boiler at 100 °C and 5 bar, and it is released as vapor at 152 °C (*stream 28*). Once in the absorbtion tower, the SO_3 cooled gases (*stream 9*) pass from bottom to top while they are absorbed by sulfuric acid (*stream 15*, ca. 150000 kg/h) of a concentration slightly higher than 78 wt%, which is irrigated from the top. The product sulfuric acid (*stream 10*) leaves the absorbtion tower with a concentration of ca. 78 wt% at 63 °C and ca. 1 bar. Then, a pump compresses the acid stream up to 1.1 bar for circulation purposes (*stream 11*). One part of this flow (*stream 12*, 2580 kg/h) is the *plant product stream*; that is, the sulfuric acid stream which is stored for later being sold. The rest of the flow is used as recirculation stream (*stream 13*).

In terms of regulating the acid concentration and acid-cooling, water (*stream 29*, ca. 528000 kg/h) at 20 °C and 1 bar is added to the process, so a pump is also needed to increase its pressure up to 1.1 bar (*stream 30*). One part of the water (stream *32*, 155 kg/h) is mixed with the recycling acid to maintain an acid outlet concentration of 78 wt%, while the rest (stream *31*, ca. 527800 kg/h) is used to cool the acid flow (stream *14*) down to 40 °C in the third heat exchanger. This water is returned to the environment at 23 °C (*stream 32*).

Stack gases (*stream 16*, 15661 kg/h) are released at 40 °C and 1 bar, sending ca. 587 kg/h of CO_2 and ca. 3.5 kg/h of SO_2 to the atmosphere.

A simplified process mass and sulphur molar balances are shown by Figures 2.3 and 2.4, respectively.

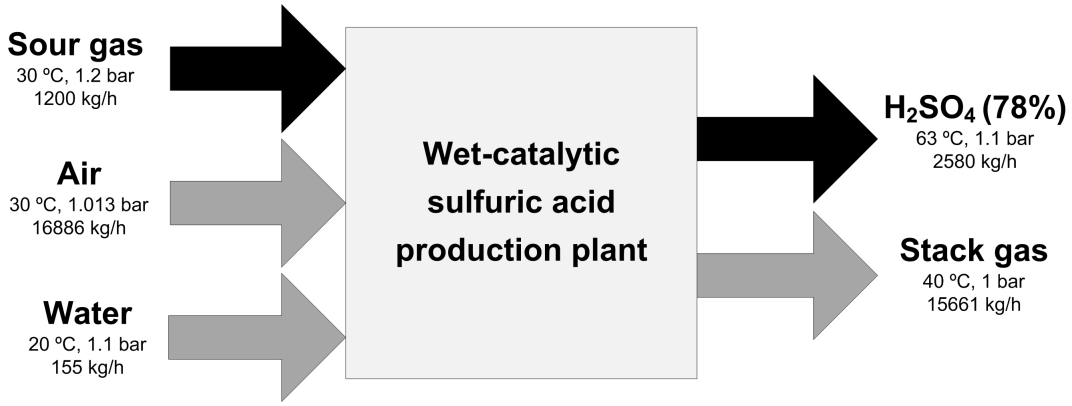


Figure 2.3: Process mass balance

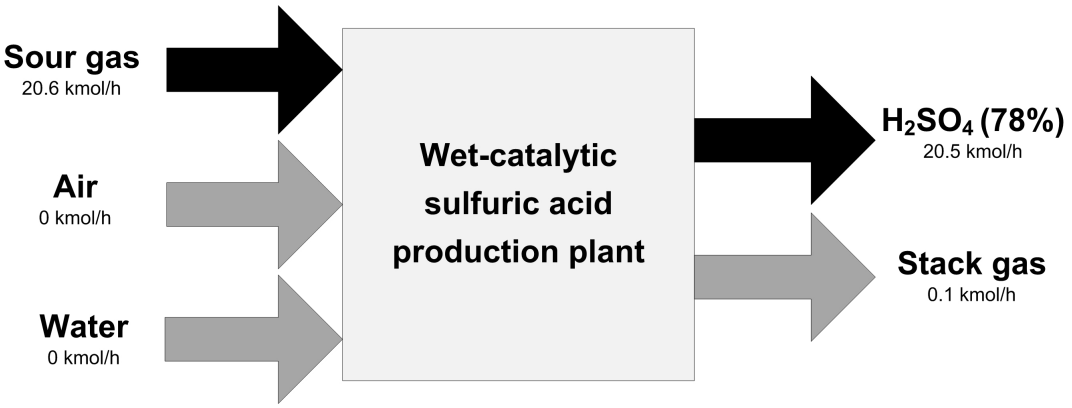


Figure 2.4: Process molar sulphur balance

The simulation needs some constrain equations in order to converge. Consequently, the process is governed by the following equations:

$$min(T_k - T_{k,set})^2 \qquad k = 2, 5, 7 \tag{2.1}$$
$$\dot{n}_{19}, \dot{n}_{21}, \dot{n}_{23}$$

$$T_{2,set} = 1200\,^{\circ}\mathrm{C} \tag{2.2}$$

$$T_{5,set} = 400\,^{\circ}\mathrm{C} \tag{2.3}$$

$$T_{7,set} = 380\,^{\circ}\mathrm{C} \tag{2.4}$$

$$\dot{n}_{9,SO_3} = \dot{n}_{12,H_2SO_4} \tag{2.5}$$

$$\dot{n}_{32} + \dot{n}_{9,H_2O} = \dot{n}_{12} + \dot{n}_{16,H_2O} \tag{2.6}$$

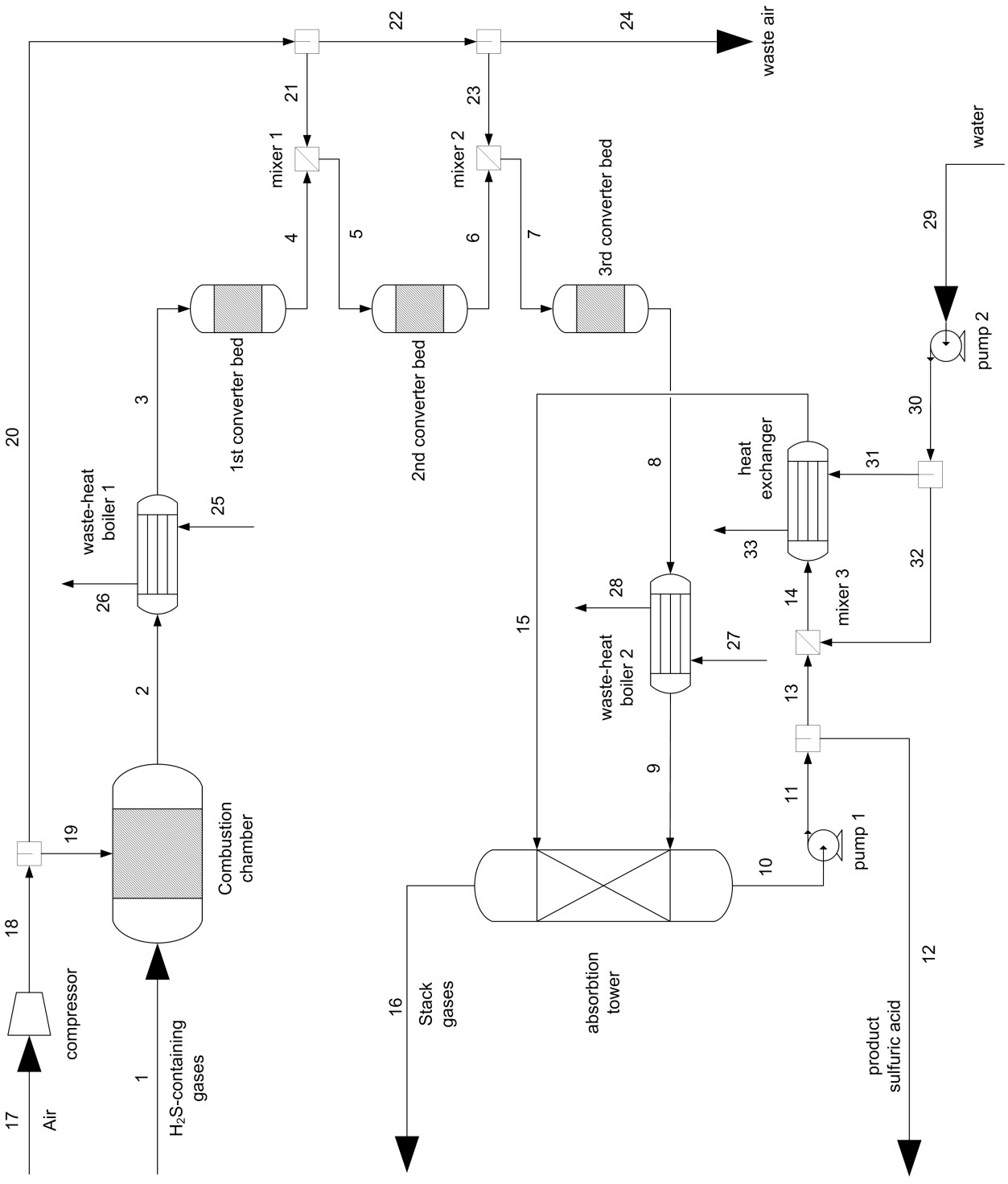


Figure 2.5: Our case study process

Equation (2.5) sets a 100% conversion of SO_3 to H_2SO_4 in the absorbtion tower, at the same time that sets the molar sulfuric acid mass stream [Equation (2.7)] due to the fact that both molar concentration of streams 9 and 12 are known. Equation (2.6) is used to set the water balance at the absorbtion stage, so the molar water stream in a steady state is not independent [Equation (2.8)].

$$\dot{n}_{12} = \dot{n}_{,Product\_acid} = \dot{n}_9 \frac{x_{9,SO_3}}{x_{12,H_2SO_4}} \tag{2.7}$$

$$\dot{n}_{32} = \dot{n}_{Water} = \dot{n}_9 \frac{x_{9,SO_3}}{x_{12,H_2SO_4}} + \dot{n}_{16,H_2O} - \dot{n}_{9,H_2O} \tag{2.8}$$

Table 2.1 shows the plant surrounding conditions. This conditions cannot be changed.

				molar composition (x_i)					
	stream nº	**T [°C]**	**P [bar]**	**N_2**	**O_2**	**H_2O**	**H_2S**	**CO_2**	**HCN**
Sour gas	1	30	1.2	0	0	0.06	0.57	0.16	0.21
Atmospheric air	17	30	1.013	0.77	0.20	0.03	0	0	0
Water to boiler I	25	100	40	0	0	1	0	0	0
Water to boiler II	27	100	5	0	0	1	0	0	0
Water	29	20	1.013	0	0	1	0	0	0

Table 2.1: Surrounding conditions

Table 2.2 shows the plant parameter temperatures. This temperatures have a strong influence on the plant's operation, since depending on their values, some processes might not be properly performed. In next chapters this is discussed carefully.

	stream nº	**T [°C]**
SO_2 from c. chamber	2	1200
SO_2 from boiler	3	400
SO_3 from quench I	5	400
SO_3 from quench II	7	380
SO_3 from boiler	9	120
H_2SO_4 from heat-exchanger	15	40

Table 2.2: Parameter temperatures

Tables 2.3 and 2.4 show the properties of all process streams: mass and molar flow rates [kg/h], [kmol/h], temperatures [°C], pressures [bar], gas molar fraction (z) [-], and flow molar composition (x_i). The bold properties mean parameter properties, while the bold-grey mean surroundings conditions.

	stream n°	ṁ [kg/h]	ṅ [kmol/h]	T [°C]	P [bar]	z	molar composition (x_i)						
							N_2	O_2	H_2O	H_2S	SO_2	SO_3	H_2SO_4	CO_2
Sour gas[1]	1	1200	36	**30**	**1.2**	**0.972**	0	0	0.0600	0.5700	0	0	0	0.1600
SO_2 from c. chamber	2	11644	390	**1200**	1.2	1	0.7324	0.0841	0.0963	0	0.0528	0	0	0.0343
SO_2 from boiler	3	11644	390	**400**	1.2	1	0.7324	0.0841	0.0963	0	0.0528	0	0	0.0343
SO_3 from horde I	4	11644	381	534	1.197	1	0.75	0.0622	0.0986	0	0.0061	0.048	0	0.0351
SO_3 from quench I	5	11645	549	**400**	1.197	1	0.7562	0.1044	0.0776	0	0.0042	0.0333	0	0.0243
SO_3 from horde II	6	11645	548	412	1.073	1	0.7577	0.1027	0.0777	0	0.0003	0.0373	0	0.0244
SO_3 from quench II	7	18086	606	**380**	1.073	1	0.7588	0.1120	0.0731	0	0.0003	0.0337	0	0.0220
SO_3 from horde III	8	18086	607	380	1.058	1	0.7589	0.1120	0.0731	0	0.0001	0.0339	0	0.0220
SO_3 from boiler	9	18086	607	**120**	1.058	1	0.7589	0.1120	0.0731	0	0.0001	0.0339	0	0.0220
H_2SO_4 from absorbtion	10	152580	3077	63	1.03	0	0	0	0.6057	0	0	0	0.3943	0
H_2SO_4 from pump	11	152580	3077	63	**1.1**	0	0	0	0.6057	0	0	0	0.3943	0
H_2SO_4 to sell	12	2580[2]	52	63	1.1	0	0	0	0.6057	0	0	0	0.3943	0
H_2SO_4 to recirculate	13	150000	3025	63	1.1	0	0	0	0.6057	0	0	0	0.3943	0
H_2SO_4 mixed with water	14	150155	3034	63	1.1	0	0	0	0.6068	0	0	0	0.3932	0
H_2SO_4 from heat-exchanger	15	150155	3034	**40**	1.1	0	0	0	0.6068	0	0	0	0.3932	0
Stack gas	16	15661	542	40	1.03	1	0.8484	0.1252	0.0016	0	0.0001	0	0	0.0246

Table 2.3: Process table: main stream; [1]Hydrogen cyanide molar composition = 0.21; [2]see Eq. 2.5

							molar composition (x_i)						
	stream n°	**ṁ [kg/h]**	**ṅ [kmol/h]**	**T [°C]**	**P [bar]**	**z**	**N_2**	**O_2**	**H_2O**	**H_2S**	**SO_2**	**SO_3**	**H_2SO_4**	**CO_2**
Atmospheric air	17	16886	592	**30**	**1.013**	**1**	0.7700	0.2000	0.0300	0	0	0	0	0
Air from compressor	18	16886	592	51	1.2	1	0.7700	0.2000	0.0300	0	0	0	0	0
Air to combustion	19	10444[1]	366	51	1.2	1	0.7700	0.2000	0.0300	0	0	0	0	0
Air	20	6442	226	51	1.2	1	0.7700	0.2000	0.0300	0	0	0	0	0
Air to quench I	21	4801[2]	168	51	1.2	1	0.7700	0.2000	0.0300	0	0	0	0	0
Air	22	1642	58	51	1.2	1	0.7700	0.2000	0.0300	0	0	0	0	0
Air to quench II	23	1642[3]	58	51	1.2	1	0.7700	0.2000	0.0300	0	0	0	0	0
Air released	24	0	-	-	-	-	-	-	-	-	-	-	-	
Water to boiler I	25	4680	260	**100**	**40**	**0**	0	0	1	0	0	0	0	0
Vapor from boiler I	26	4680	260	250	**40**	**1**	0	0	1	0	0	0	0	0
Water to boiler II	27	2134	118	**100**	**5**	**0**	0	0	1	0	0	0	0	0
Vapor from boiler II	28	2134	118	152	**5**	**1**	0	0	1	0	0	0	0	0
Water	29	527939[4]	29306	**20**	**1**	**0**	0	0	1	0	0	0	0	0
Water from pump	30	527939	29306	20	**1.1**	0	0	0	1	0	0	0	0	0
Water to heat exchanger	31	527784	29297	20	**1.1**	0	0	0	1	0	0	0	0	0
Water to mixer 3	32	155	8.58	20	**1.1**	0	0	0	1	0	0	0	0	0
Water from heat exchanger	33	527784	29297	23	**1.1**	0	0	0	1	0	0	0	0	0

Table 2.4: Process table: atmospheric air and water; [1]see Eq. 2.2; [2]see Eq. 2.3; [3]see Eq. 2.4; [4]see Eq. 2.6

Chapter 3

Exergy Analysis

The standard way of life on Earth has been achieved and is maintained by the exploitation of natural resources that have been accumulated over the millennia. Those natural resources which differ substantially in terms of chemical composition from the dead states of the elements comprising the resource (e.g., fossil fuels) are the most valuable insofar as they can feed and drive thermal and chemical processes. The level of consumption far exceeds the rate of replacement and eventual shortages are inevitable. For this reason, it is apparent the importance of developing thermal systems that make effective use of nonrenewable resources such as oil, natural gas, and coal.

The energy balance, based on the first law of the thermodynamics, is used in any attempt to reduce heat losses or enhance heat recovery. However, such a balance gives no information on the degradation of energy that occurs in the process, nor does it qualify the usefulness of the heat content in the various streams leaving the process as product, waste, or coolant. So, the idea of having something that can be destroyed could be useful in terms of the design and analysis of thermal systems. This idea does not apply to energy, since it is conserved, but to exergy -a second-law concept. Moreover, it is exergy and not energy that properly gauges the quality of a stream of matter. In this way, the exergy method of analysis overcomes the limitations of the first law of thermodynamics, since this concept is based on the first and also the second law. Its application indicates clearly the location, types, and true magnitudes of waste and loss in a process that may lead to design and analyze thermal systems; besides guiding efforts to reduce sources of inefficiency in existing systems, and evaluate systems economics. Further, 1J of a rejected fuel

stream which its composition at 500 °C yields 0.614 J of work, at 50 °C yields 0.077 J of work [13]. So it can be said that the first stream has a higher quality than the second.

Picture 3.1 shows us that energy and exergy are fundamentally different concepts, although they share common units. At Figure 3.1, the energy and exergy transfer rates for a control volume at steady state are shown. In accord with the conservation of energy principle, the total rate at which energy enters the control volume *equals* the total rate at which energy exits. However, the total exergy that enters the control volume *exceeds* the total rate of exiting exergy. Accordingly, exergy gives a sharper picture of performance than energy because exergy expresses all energy transfers on a common basis and accounts explicitly for the effect of irreversibilities through the exergy destruction concept.

Hence, exergy has become an increasingly important tool for the design and analysis of thermal systems. The wider application of the exergy method of analysis can lead to a substantially reduced rate in the use of natural resources and pollution of resource consumption. Exergy is also important because it provides the basis for the discussion of thermoeconomics, as it will be studied in next chapters.

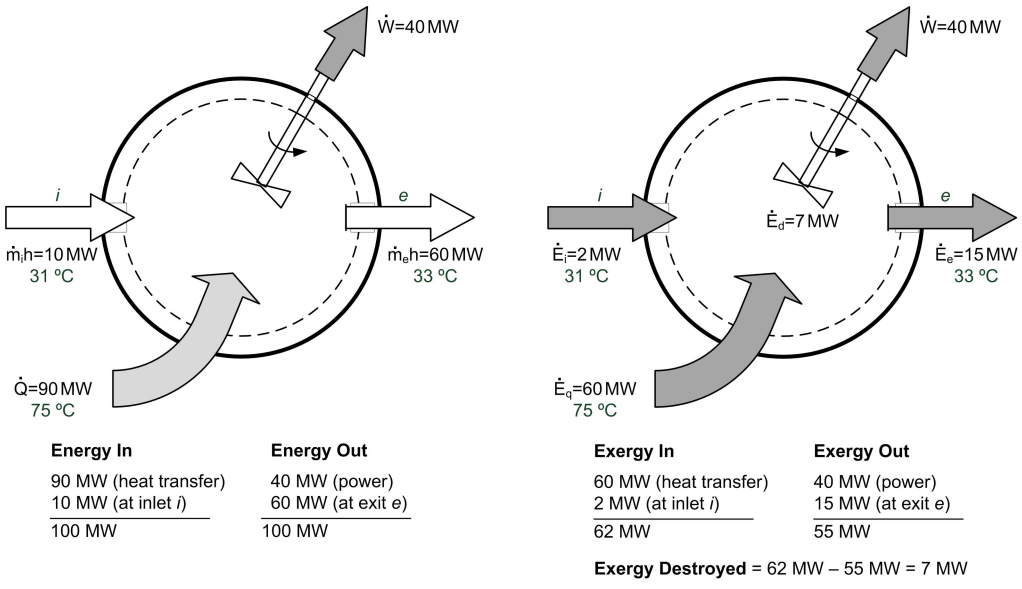


Figure 3.1: Energy v.s. Exergy

3.1 The Exergy Concept

Energy is conserved in every device or process. It cannot be destroyed. Consequently, energy entering a system with fuel, electricity, flowing streams of matter, and so on can be accounted for in the products and by-products. However, the energy conservation idea alone is inadequate for depicting some important aspects of resource utilization.

Whenever two systems are at different states and they are brought together to the equilibrium, there is always an opportunity for doing useful work. When one of these two systems is some system of interest and the other is an idealized system called *environment*, *exergy* is the maximum theoretical useful work obtainable as the system interact to equilibrium (passes to *dead state*); heat transfer occurring with environment only. This work could be lifting a weight, shaft work, or electrical work. Alternatively, exergy is the minimum theoretical useful work required to form a quantity of matter from substances present in the environment and to bring the matter to a specified state. Therefore, in order to calculate exergy, the environment must have been previously specified. As a result of that, once the environment is specified, exergy can also be considered as a property of the system.

In contrast to energy, exergy is exempt from the law of conservation. Every irreversible phenomenon causes exergy losses leading to the reduction of the useful effects of the process. Subsequent discussion shows that exergy not only can be destroyed by irreversibilites but also can be transferred to and from systems. Exergy transferred from a system to its surroundings without use, typically represents a loss. Improved energy resource utilization can be realized by reducing exergy destruction and/or reducing losses within a system. An objective in exergy analysis is to identify sites where exergy destructions and losses occur and rank-order them for significance (quantity-cost, Chapter 5), so attention can be centered on aspects of systems operation that offer the greatest opportunities for cost-effective improvements.

3.1.1 Environment and Dead States

Environment

For thermodynamic analysis involving the exergy concept, it its necessary to model the atmosphere used in the foregoing discussion. The resulting model is called the *exergy reference environment*, or simply the *environment*. The term *environment* applies to some portion of the surroundings (everything not included in the system) in which the intensive properties of each phase are uniform and do not change significantly as a result of any process under consideration. Additionally, it is regarded as free of irreversibilites.

The environment is normally considered as composed of common substances existing in abundance within the Earth's atmosphere, oceans, and surface. The substances are in their stable forms as they exist naturally, and there is no possibility of developing work from interactions -physical or chemical, as it will explained in next section- between parts of the environment. At the discussion of chemical exergy (Section 3.2.2), it will be debated which Earth's substances are taken into consideration in our system environment and which not. We will model the environment as a compressible system with an uniform temperature T_o and pressure P_o, which for simplicity at this work are taken as typical environmental conditions such as 25 °C and 1 atm (1.013 bar).

Dead States

It is said that the system stands at *dead state* (Figure 3.2) when its pressure, temperature, composition, velocity, or elevation are equal to these corresponding environment parameters. Therefore, as the system changes state toward that of the environment, the opportunity of producing useful work diminishes, ceasing when the system and the environment are in equilibrium. At this state, there is no possibility of a spontaneous change within the system or the environment, nor can there be an interaction between them. In terms of exergy, at this state the system presents exergy zero.

It must be clarified that between an ordinary system state and the dead state, there is an intermediate equilibrium level which should be also mentioned. This state is called *restricted dead state* (Figure 3.2). At this point, the system stands

only in mechanical and thermal equilibrium with the environment, so it can still produce chemical work while interacting chemically with the environment. At the restricted dead state and in order to reach the dead state, the system must interact chemically with the environment substances. Therefore, what technically happens between the restricted dead state and the dead state is that our system component concentrations are "mixed" into the environment concentrations, which says that chemical reactions take place to the equilibrium.

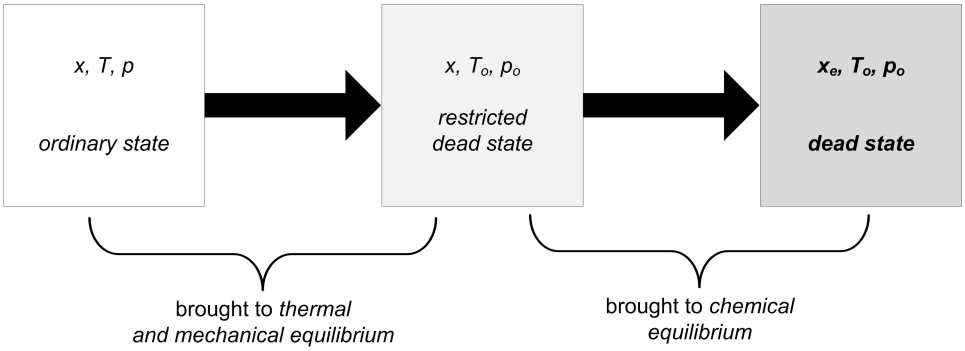


Figure 3.2: System dead states

3.2 The Exergy Components

Exergy can be divided into four components: physical E^{PH}, kinetic E^{KN}, potential E^{PT} and chemical exergy E^{CH}. The sum of the physical, kinetic and potential exergy is also known as *thermomechanical exergy*. The sum of the thermomechanical and chemical exergy is the *total exergy* associated with a given system at a specified state, relative to a specified exergy reference environment.

$$E = E^{PH} + E^{KN} + E^{PT} + E^{CH} \tag{3.1}$$

However, at this work, only the physical and chemical exergy will be taken into consideration, since our system case process is considered at rest relative to the environment and then the kinetic and potential exergies have zero value. So, from now on, when it is talked about exergy or total exergy it will refer to the sum of only the physical and chemical exergy.

$$E = E^{PH} + E^{CH} \tag{3.2}$$

For this work, an add-on tool called CHEMEX was designed for calculating physical and chemical exergy from a desired process stream in CHEMCAD, a commercial flow sheet simulator. CHEMEX was programmed in Fortran and more information about this program can be found in the Appendix C. Table 3.1 and Table 3.2 show the exergy rate values of all system streams, as well as enthalpy and mass and molar exergy rate values.

3.2.1 Physical Exergy

Physical exergy, E^{PH}, is the work obtainable by taking the substance through reversible physical processes from its initial state temperature T and pressure P, to the restricted dead state determined by the temperature T_o and pressure P_o of the environment. The physical exergy of a closed system at a specified state is given by the expression

$$E^{PH} = (U - U_o) + P_o(V - V_o) - T_o(S - S_o) \tag{3.3}$$

Where U, V, and S denote, respectively, the internal energy, volume, and entropy of the system at the specified state, and U_o, V_o, and S_o are the values of the same properties when the system is at the restricted dead state.

Since the environment pressure, P_o, remains always constant, Equation (3.3) can be rewritten as it follows:

$$E^{PH} = (H - H_o) - T_o(S - S_o) \tag{3.4}$$

Here, H and H_o mean the enthalpy of the system at the specified state, and at the restricted dead state, respectively. This expression apart of being more compact than the first one, it is more comfortable for calculating the physical exergy, since CHEMCAD can easily calculate enthalpy and entropy values from a desired process stream. Then, CHEMEX must only import this data and calculate the physical exergy value.

3.2.2 Chemical Exergy

Chemical exergy is the maximum work that can be obtained by taking a substance having the environment parameters T_o, P_o, to the thermodynamic equilibrium, or dead state, with the substances which comprise the environment. At dead state,

the substance, now a part of the environment, have the new partial pressure $x_e P_o$, which can be denoted by P_{oo}. Where x_e, shown in Figure 3.2, refers to the molar fraction of the substance in the environment. Equation (3.5) quantifies analytically the chemical exergy per mole of a substance, also known as *standard chemical exergy.*

$$\overline{e}^{CH} = RT_o \ln \frac{P_o}{P_{oo}} = -RT_o \ln x_e \tag{3.5}$$

In practice, the values calculated through Equation (3.5) can be found in published tables for different chemical elements, depending on the environmental model [6, 13], usually in kJ/kmol, determined relative to an *standard environment* at temperature T_o and pressure P_o. For simplicity, a temperature of 25 °C and a pressure of 1 atm are usually used as reference environment conditions, since the effect of slight variations in them can be neglected [13].

A standard environment could be defined as a suitably selected set of reference substances with standard concentrations reflecting as closely as possible the chemical makeup of the natural environment, where these reference substances must be in mutual equilibrium to exclude the possibility of developing work from interactions between parts of the environment.

Two alternative standard exergy reference environments are commonly used, *Model I* [6] and *Model II* [13], each of them reflecting the environment composition in a different way. Only one of the two models should be used in a particular analysis. At this work it is used the Model I. However, CHEMEX offers also the possibility to choose the Model II for further studies. On one hand, Model I attempts to satisfy the equilibrium requirement of the thermodynamic theory; that is, the gas phase of this model approximates properly the chemical composition of the natural atmosphere. On the other hand, Model II approximates better the chemical composition of the overall natural environment, but the equilibrium requirement is not satisfied as in Model I [5].

In order to calculate the chemical exergy of a gas mixture, the following equation is used:

$$e_M^{CH} = \sum z_k \overline{e}_k^{CH} + RT_o \sum z_k \ln z_k \tag{3.6}$$

Where e_M^{CH} is the total molar chemical exergy of the mixture; $\overline{e}_k^{CH}$ and z_k are the standard chemical exergy and the gas molar fraction of the k-th component in the mixture, respectively; R is the molar universal gas constant (8.314 kJ kmol^{-1} K^{-1}).

In order to calculate the chemical exergy of a liquid solution, the following equations is used:

$$e_M^{CH} = \sum y_k \bar{e}_k^{CH} + RT_o \sum y_k \ln \gamma_k y_k \tag{3.7}$$

Where here y_k and γ_k denotes the liquid molar fraction and activity coefficient of the k-th component in the solution, respectively. The activity coefficient is an dimensionless coefficient which expresses how strong a solution differs from its ideal case. For *ideal solutions* activity coefficients are unity and may be greater or smaller than unity for *real solutions*. At this work, it is only taken into account the activity coefficients of water and sulfuric acid, since both components are strongly reactive. The calculation of the activity coefficients is discussed in the next section.

Activity Coefficient Calculation

For a nonideal solution, the molar free energy, g, is the sum of the molar free energy of an ideal solution and an excess molar free energy g^E, describing the nonideal effects. For a liquid solution,

$$g = \underbrace{\sum_i y_i g_i + RT \sum_i y_i \ln y_i}_{ideal solution} + g^E \tag{3.8}$$

where $g \equiv h - Ts$ and the excess molar free energy, g^E, is the the sum of the partial excess molar free energies. The partial excess molar free energy is related by classical thermodynamics to the liquid-phase activity coefficient by the following equation [16]:

$$\frac{g_i^E}{RT} = \ln \gamma_i = \frac{g^E}{RT} - \sum_k y_k \left[\frac{\partial (g^E/RT)}{\partial y_k} \right]_{p,T,y_r} \tag{3.9}$$

where r $\neq$ k, k $\neq$ i, and r $\neq$ i.

In this thesis, only the activity coefficients of water and sulfuric acid are calculated in liquid solutions (*process streams 10, 11, 12, 13, 14, and 15*). Recalculated this binary mixture in Equation (3.9) leads to Equations (3.10) and (3.11) [19].

$$\ln \gamma_{H_2O} = \frac{g^E}{RT} - \frac{y_{H_2SO_4}}{RT} \frac{\partial g^E}{\partial y_{H_2SO_4}} \tag{3.10}$$

$$\ln \gamma_{H_2SO_4} = \frac{g^E}{RT} - \frac{(1 - y_{H_2SO_4})}{RT} \frac{\partial g^E}{\partial y_{H_2O}} \tag{3.11}$$

CHEMEX calculates the activity coefficients of water, γ_{H_2O}, and sulfuric acid, $\gamma_{H_2SO_4}$, using a 6-th grade polynomial function approximation for the excess molar free energy [32]. In Appendix C, the activity coefficient calculation with CHEMEX is explained in detail.

Figures 3.4 and 3.5 expose results from program calculations for a binary solution H_2SO_4/H_2O at environmental conditions (25 °C and 1.013 bar), since chemical exergy is calculated at the dead state. In Figure 3.4, it can be observed that at low acid concentrations γ_{H_2O} is close to the unity and $\gamma_{H_2SO_4}$ to zero; while at high acid concentrations it happens the opposite. This means that when the solution tends to be formed by only one component, its behavior is near the ideal case, since there is not interaction between both components. Otherwise, when the solution presents a molar concentration between 30 and 50% sulfuric acid, the strongest interaction between the two components is reached. This fact can be properly observed in Figure 3.5.

In the reference process, there are only two cases of different activity coefficient values: one according to a molar concentration of 0.3943 (*flows 10, 11, 12 and 13*) and the another to 0.3932 % sulfuric acid (*flows 14 and 15*) (Table 3.3).

	stream n^{o}	γ_{H_2O}	$\gamma_{H_2SO_4}$
H_2SO_4 from absorbtion	10	0.0058146	0.0056909
H_2SO_4 from pump	11	0.0058146	0.0056909
H_2SO_4 to sell	12	0.0058146	0.0056909
H_2SO_4 to recirculate	13	0.0058146	0.0056909
H_2SO_4 mixed with water	14	0.0059621	0.0054756
H_2SO_4 from heat-exchanger	15	0.0059621	0.0054756

Table 3.3: Activity coefficients

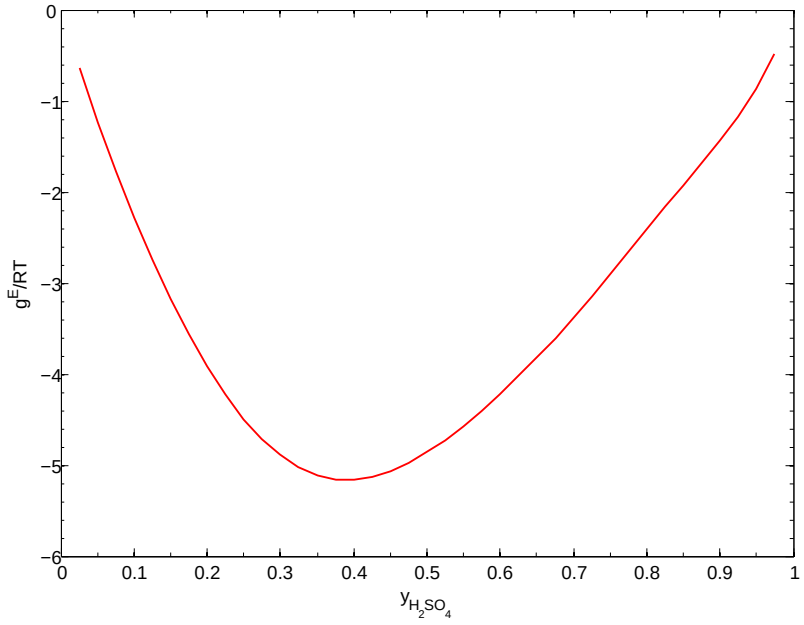


Figure 3.3: Excess molar free energy g^E in a liquid mixture H_2O/H_2SO_4 (78 wt%) for or the overall range of $y_{H_2SO_4}$, at 25 °C and 1.013 bar

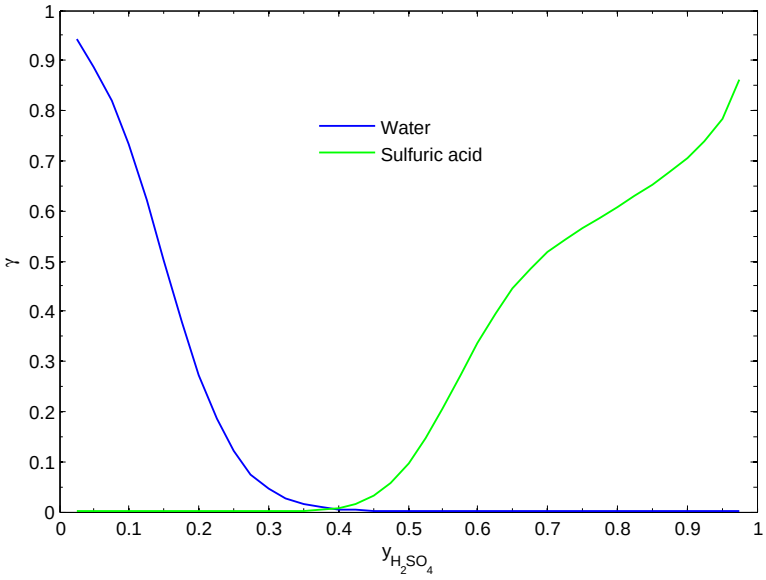


Figure 3.4: Activity coefficients for H_2O and H_2SO_4, $y_{H_2SO_4} \in (0,1)$, at 25 °C and 1.013 bar

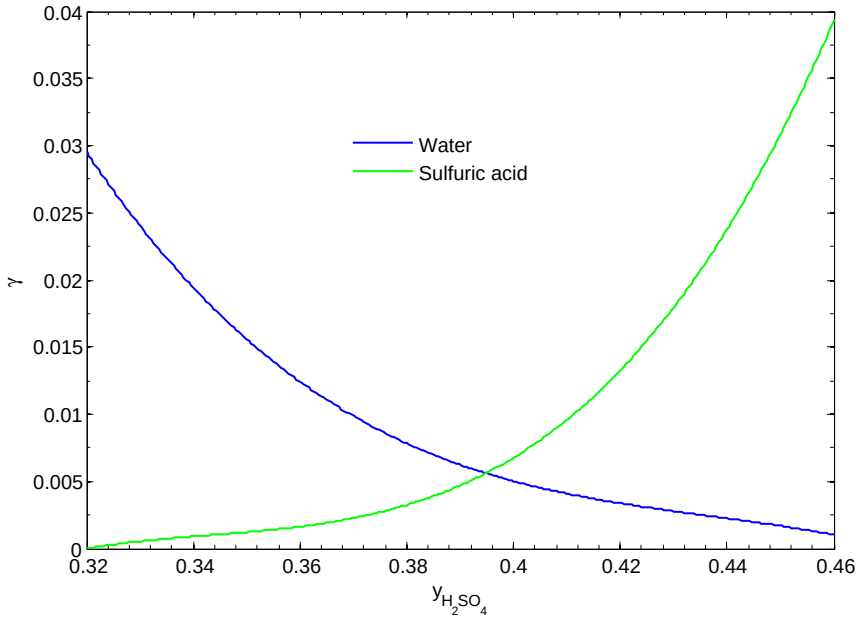


Figure 3.5: Activity coefficients for H_2O and H_2SO_4, $y_{H_2SO_4} \in (0.3,0.5)$, at 25 °C and 1.013 bar

3.3 Exergy Rate Balance for Control Volumes at Steady State

Since the analysis considered in this work involve control volumes at steady state, it is important to know the steady-state form of the exergy rate balance. At steady state, the exergy rate balance of a control volume can be expressed as

$$0 = \sum_j \dot{E}_{q,j} - \dot{W}_{CV} + \sum_i \dot{E}_i - \sum_e \dot{E}_e - \dot{E}_D \tag{3.12}$$

where $\dot{E}_{q,j}$ is interpreted as the exergy transfer rate associated with the transfer of energy by heat; $\dot{W}_{CV}$ represents the time rate of energy transfer by work; $\dot{E}_i$ and $\dot{E}_e$ are exergy transfer rates at inlets and outlets, respectively; and $\dot{E}_D$ accounts for the time rate of exergy destruction due to irreversibilities within the control volume. The exergy destruction concept is discussed in the next section.

Support equations:

$$\dot{E}_{q,j} = (1 - \frac{T_o}{T_j})\dot{Q}_j \tag{3.13}$$

$$\dot{E}_i = \dot{n}_i \overline{e}_i \tag{3.14}$$

$$\dot{E}_e = \dot{n}_e \overline{e}_e \tag{3.15}$$

where T_j denotes the temperature on the boundary where energy transfer by heat occurs; $\overline{e}_i$ accounts for the molar exergy entering at inlet i and $\overline{e}_e$ accounts for the molar exergy exiting at exit e.

Equation (3.12) states that the sum of the rates at which exergy and heat are transferred into the control volume is divided into the rate at which is transferred out, the work that is produced within, and the rate at which exergy is destroyed.

3.4 Exergy Destruction and Loss

As commented in previous sections, the exergy destruction and the exergy loss are the principal aim to any exergy analysis, since they represent the waste of the resources, for example fossil fuels, consumed in a thermal/chemical system. Accordingly, better use of fuels can be made by conceiving ways to reduce such inefficiencies. The exergy balance can be applied to determine the locations, types, and true magnitudes of energy resource waste, and thus it plays an important part in developing strategies for more effective fuel use.

For a system at steady state, the following exergy balance can be derived from Equation (3.12) (see Section 3.3)

$$\dot{E}_i + \dot{E}_q = \dot{E}_e + \dot{W} + \dot{E}_D + \dot{E}_L \tag{3.16}$$

where $\dot{E}_i$ and $\dot{E}_e$ mean the entering and exiting exergy flow rates, respectively; $\dot{E}_q$ is the exergy by heat transfer (>0 for entering heat), $\dot{W}$ the work transfer rate (>0 for work done by the system), and $\dot{E}_D$ the exergy destruction in the system; $\dot{E}_L$ represent the exergy losses. When the system is a control volume for one of our acid plant components, the last two terms in Equation 3.16 are strongly of interest, since they can be reduced and consequently the component can be improved. The first of them, the exergy destruction, is the most important result of the exergy analysis and it represents the exergy rate which has been destroyed by irreversibilities due to processes inside the system. So our principle aim is to reduce this term in each acid plant component balance. These reductions are always done taking into account the costs that they involve, as it is shown in next chapters.

The exergy destruction rate can be determined by Equation (3.17), $\dot{E}_{D(a)}$, or by means of the system balance [Equation (3.16)], $\dot{E}_{D(b)}$. Both methodologies are used

in this thesis in order to verify the results of exergy calculation approaches presented in Section 3.3.

$$\dot{E}_D = T_o \dot{S}_{gen} \tag{3.17}$$

where $\dot{S}_{gen}$ is the entropy generation, in this case of the overall system process (see Figure 3.6). The term $\dot{S}_{gen}$ can be calculated with the following entropy rate balance at steady state

$$0 = \sum_j \frac{\dot{Q}_j}{T_j} + \sum_i \dot{S}_i - \sum_e \dot{S}_e + \dot{S}_{gen} \tag{3.18}$$

where here the term $\dot{Q}_j$ represents the time rate of heat transfer at the location on the boundary where the instantaneous temperature is T_j, and $\dot{S}_i$ and $\dot{S}_e$ are the entering and exiting entropy flow rates, respectively. The ratio $\frac{\dot{Q}_j}{T_j}$ accounts for the associated rate of entropy transfer by heat transfer. Figure 3.6 shows all type of our acid plant components with its corresponding entropy generation [Equation (3.18)] and exergy destruction definitions [Equation (3.16)].

The second term of interest, the exergy losses, consists of the exergy rates from system-leaving streams. For that reason it is called exergy losses, since these exergies leaving the system could be used, but they are wasted. Nevertheless, this type of streams are not studied in component exergy balances, but rather in an exergy balance of the overall process. Once that clarified, by reducing these leaving exergy flow rates from the overall process, the performance of our sulfuric acid plant can be improved as well. The system exergy losses are basically allocated in flows *16* (Stack gasses) and *13* (cooling water leaving the third heat exchanger) with a value of 0.04 kW and 0.36 kW (Tables 3.1 and 3.2), respectively. Stream *24* is also an exergy loss, but it is not considered since it presents a zero mass rate. Table 3.4 shows the exergy destruction rates from each system component of the acid plant, calculated by the two methods described in this section and with its correspondingly absolute and relative errors [Equations (3.19) and (3.20)]. The exergy destruction calculated through the entropy generation method is taken as a reference for the error calculation, since flow entropies in CHEMCAD are precisely calculated using the *NRTL model* [7]. Consequently, the error gauges the quality of the results calculated through the balance method and further, the quality of the approaching for the activity coefficient.

$$\epsilon_{abs} = |\dot{E}_{D(a)} - \dot{E}_{D(b)}| \tag{3.19}$$

$$\epsilon_{rel} = \frac{\epsilon_{abs}}{\dot{E}_{D(a)}} \cdot 100 \tag{3.20}$$

The highest relative errors come from pump 1 with a value of 95.9%. The reason is that the exergy destruction calculated through the exergy balance in the pump consists only of a difference between two close values (exergies from flows *10* and *11*), since work rates can be neglected due to its small value in comparison with the other exergy values in the balance (see Figure 3.6). In such cases, CHEMCAD commits precision errors. In the case of pump 2, the relative error cannot be considered, since the entropy difference between flows *30* and *29* is zero. That happens also due to CHEMCAD precision errors by calculating the entropy for streams which present similar properties (flows *29* and *30*).

The next two highest relative errors are located in the absorbtion column and the first converter bed with values of 9.69 and 10.6%, respectively. The main reason is related to the chemical reaction in both system components; that is, the conversion of SO_2 into SO_3 in the converter, and the absorbtion of SO_3 in H_2SO_4 in the absorbtion column. Here, the differences between the two methodologies are stronger than in other system components because of the elevated influence of the activity coefficients in the exergy balances. The reason is that the first exergy destruction method, which uses the NRTL model, takes into account all activity coefficients of all the substances present in each flow, while the second only the activity of water and sulfuric acid, as explained in Section 3.2.2. The activity coefficient of SO_3 is an example of an activity coefficient which is not taken into account in the balance method, but however its influence should not be neglected. Although the entering and exiting flows in the catalytic conversion of the process present only a gas phase, the calculation of the activity coefficient is performed always under environmental conditions (25 °C and 1.013 bar), so the flow could yield also a liquid phase and thus, a non-depreciable SO_3/H_2O-activity. This phenomenon can be significantly appreciated in the first contact bed, where the effect of not taking into account the SO_3-activity coefficient is stronger than in the second and third beds because of the fact that there is a bigger difference between the entering and exiting flow's composition in terms of chemical exergy. Equation (3.21) shows analytically the difference between both types of

exergy destruction calculations (entropy generation/balance). Consequently, taking into account that in the working range the activity coefficient of SO_3 and H_2O are not higher than the unity [32], the difference between both methodologies presents positive sign. In the second and third beds, this difference is decreasingly smaller ($\epsilon_{abs,bed1}$=1.17 kW; $\epsilon_{abs,bed2}$=0.32 kW), since the effect of the SO_3/H_2O-activity is not only present in the bed's outlet flow (first contact bed), but in both inlet and outlet flows.

$$\begin{aligned} \dot{E}^{bed1}_{D,(a)} - \dot{E}^{bed1}_{D,(b)} \sim \dot{E}^{bed1}_{CH,(a)} - \dot{E}^{bed1}_{CH,(b)} \sim \\ \sim RT_o \left(\sum y_k \ln \gamma_k y_k\right)_{(a)} - RT_o \underbrace{\left(\sum y_k \ln \gamma_k y_k\right)_{(b)}}_{0} \sim \\ \sim -RT_o \left(\ln \gamma_{H_2O} y_{H_2O} + \ln \gamma_{SO_3} y_{SO_3}\right)_{(a)} \sim \epsilon_{abs,bed1} = 4.86\ kW \end{aligned} \tag{3.21}$$

In the other system components, errors are justified by both precision errors of CHEMCAD and for not taking into account all activity coefficients.

3.5 Exergy ratios

For being capable of comparing from an exergetic point of view, and having a more accurate idea about how exergy is distributed in a process plant, it is useful to define exergy ratios as the *exergy destruction ratio*, the *exergy loss ratio*, and the *exergetic efficiency*.

3.5.1 Exergetic efficiency

The exergetic efficiency is a parameter for evaluating thermodynamic performance and provides a true measure of the performance of an energy system from the thermodynamic point of view.

In defining the exergetic efficiency it is necessary to identify both a product and a fuel for the thermodynamic system being analyzed. The product represents the desired result produced by the system. The fuel represents the resources expended to generate the product, and it is not necessarily restricted to be an actual fuel such as natural gas, oil, or coal. However, it must be taken into account that for some thermodynamic systems it is not possible to define an exergetic efficiency or at least it does not have any sense, since the products and fuels are not clearly known. In

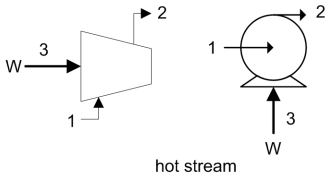
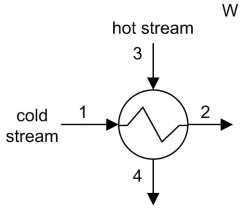
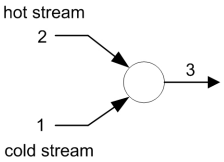
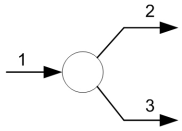
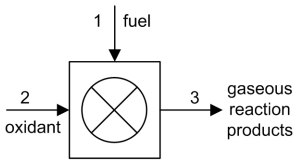
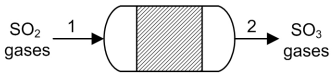
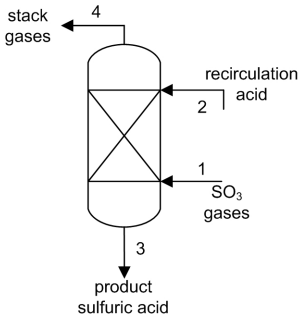
Component	Schematic	Entropy generation S_{gen}	Exergy destruction E_D
Compressor and pum		S_2-S_1	E_1+W_3-E_2
Heat exchanger		(S_2+S_4)-(S_1+S_3)	(E_1+E_3)-(E_2+E_4)
Mixer		S_3-(S_2+S_1)	(E_1+E_2)-E_3
Divider		0	0
Adiabatic Combustion chamber		S_3-(S_2+S_1)	(E_1+E_2)-E_3
Adiabatic Contact horde		S_2-S_1	E_1-E_2
Adiabatic Absorbtion column		(S_3+S_4)-(S_1+S_2)	(E_1+E_2)-(E_3+E_4)

Figure 3.6: Entropy generation and exergy destruction for each component type in the reference acid plant

this work that happens with some system components such as converters and the absorbtion column. Therefore, it will be only defined the overall system exergetic efficiency. For that, using Equation (3.12), the overall system exergetic efficiency is

defined as

$$\Psi = \frac{\dot{E}_{P,tot}}{\dot{E}_{F,tot}} = 1 - \frac{\dot{E}_{D,tot} + \dot{E}_{L,tot}}{\dot{E}_{F,tot}} \tag{3.22}$$

The product consists of the sum of the *sulfuric acid to sell (stream 12)* exergy and the exergetic increment of the *high-pressure steam* (differences between *streams 26 and 25*; and between *streams 28 and 27*). The fuel consists of the sum of the *hydrogen sulfide (stream 1)* exergy, the *atmospheric air* (*stream 17*) exergy, the *system water (stream 29)* exergy, and the work rates from the *compressor* and the *pumps* (see Table 3.5).

$$\Psi = \frac{\dot{E}_{12} + (\dot{E}_{26} - \dot{E}_{25}) + (\dot{E}_{28} - \dot{E}_{27})}{\dot{E}_1 + \dot{E}_{17} + \dot{E}_{31} + \dot{W}_{comp} + \dot{W}_{pumps}} \tag{3.23}$$

$$\Psi = \frac{2.35}{6.40} = 0.367 \rightarrow 36.7\% \tag{3.24}$$

The exergetic efficiency (36.7%) shows the percentage of the product exergy that is found in the fuel exergy provided to a system. An important use of exergetic efficiencies is to assess the thermodynamic performance of a component, plant, or industry relative to the performance of similar components, plants, or industries. From literature [18], it is known that a sulfuric acid plant which consists of a sulfur-burning contact process has an overall exergetic efficiency of 47.2%. This process is basically composed of the following components: a sulphur burner, an economizer, two waste heat boilers (50 bar), two converter beds, a gas cooler (gas/gas heat exchanger), an absorbtion column, and an acid cooler (liquid/air heat exchanger). Heat losses and pressure losses are neglected.

3.5.2 Exergy Destruction and Exergy Loss Ratios

The rates of exergy destruction $\dot{E}_D$ and exergy loss $\dot{E}_L$ provide thermodynamic measures of the system inefficiencies. The exergy destruction ratio y_D in a system component is defined as the ratio between the exergy destruction rate within and the exergy rate of the fuel provided to the overall system

$$y_D = \frac{\dot{E}_D}{\dot{E}_{F,tot}} \tag{3.25}$$

Alternatively, the component exergy destruction rate can be compared to the total exergy destruction rate within the system, $\dot{E}_{D,tot}$, giving the ratio

$$y_D^* = \frac{\dot{E}_D}{\dot{E}_{D,tot}} \tag{3.26}$$

The two exergy destruction ratios are useful for comparisons among various components of the same system, or among similar components of different systems using similar fuels.

The exergy loss ratio is defined comparing the exergy loss to the exergy of the fuel provided to the overall system

$$y_L = \frac{\dot{E}_L}{\dot{E}_{F,tot}} \tag{3.27}$$

In the sulfuric acid plant, the exergy losses are basically due to the streams *16* and *33*, leading to an exergy loss ratio of 6.1% (Equation 3.28).

$$y_L = \frac{\dot{E}_{16} + \dot{E}_{33}}{\dot{E}_{F,tot}} = \frac{0.04 + 0.36}{6.40} = 0.061 \rightarrow 6.1\% \tag{3.28}$$

Table 3.6 shows the exergy destruction rates arranged in order decreasingly from each system component of the acid plant, calculated by the two methods described in Section 3.4, as well as the exergy loss ratio.

	stream nº	$\dot{\mathbf{H}}$ **[kW]**	$\dot{\mathbf{S}}$ **[kW/K]**	$\dot{\mathbf{E}}_{PH}$ **[kW]**	$\dot{\mathbf{E}}_{CH}$ **[kW]**	$\dot{\mathbf{E}}$ **[kW]**	**e [MJ/kg]**	$\bar{\mathbf{e}}$ **[MJ/kmol]**
Sour gas	1	-620	0.34	3.87	5938	5.94	17.83	592
SO_2 from c. chamber	2	-1283	6.01	2743	1689	4.43	1.37	40.89
SO_2 from boiler 1	3	-4396	3.00	531	1689	2.22	0.69	20.48
SO_3 from horde 1	4	-4396	3.15	832	1347	2.18	0.67	20.58
SO_3 from quench 1	5	-4700	3.79	739	1331	2.07	0.45	13.56
SO_3 from horde 2	6	-4700	3.94	732	1295	2.03	0.44	13.31
SO_3 from quench 2	7	-4804	4.14	703	1291	1.99	0.40	11.85
SO_3 from horde 3	8	-4804	4.16	699	1290	1.99	0.40	11.80
SO_3 from boiler 2	9	-6199	1.44	113	1290	1.40	0.28	8.32
H_2SO_4 from absorbtion	10	-429524	-198	338	38651	38.99	0.92	45.62
H_2SO_4 from pump	11	-429524	-198	338	38651	38.99	0.92	45.62
H_2SO_4 to sell	12	-7263	-3.35	5.72	654	0.66	0.92	45.62
H_2SO_4 to recirculate	13	-422261	-195	332	37997	38.33	0.92	45.62
H_2SO_4 mixed with water	14	-422942	-195	334	37964	38.30	0.92	45.45
H_2SO_4 from heat-exchanger	15	-424781	-201	102	37964	38.07	0.92	45.78
Stack gas	16	-1456	0.82	7.29	29	0.04	0.01	0.24

Table 3.1: Exergy table: main stream

	stream nº	$\dot{H}$ [kW]	$\dot{S}$ [kW/K]	$\dot{E}_{PH}$ [kW]	$\dot{E}_{CH}$ [kW]	$\dot{E}$ [kW]	e [MJ/kg]	$\bar{e}$ [MJ/kmol]
Atmospheric air	17	-1169	0.68	0.15	-2.67	0.00	0.00	-0.02
Air from compressor	18	-1071	0.77	71.5	-2.67	0.07	0.01	0.42
Air to combustion	19	-662	0.48	44.2	-1.65	0.04	0.01	0.42
Air	20	-408	0.29	27.3	-1.02	0.03	0.01	0.42
Air to quench 1	21	-304	0.22	20.32	-0.76	0.02	0.01	0.42
Air	22	-104	0.07	6.95	-0.26	0.01	0.01	0.42
Air to quench 2	23	-104	0.07	6.95	-0.26	0.01	0.01	0.42
Air released	24	0	-	-	-	-		
Water to boiler 1	25	-20230	-10.54	44.36	3.25	0.05	0.04	0.66
Vapor from boiler 1	26	-17117	-4.35	1312	3.25	1.31	1.01	18.22
Water to boiler 2	27	-9225	-4.80	20.24	1.48	0.02	0.04	0.66
Vapor from boiler 2	28	-7829	-1.54	441	1.48	0.44	0.75	13.45
Water	29	-2331308	-1336	-10.71	366	0.36	0.00	0.04
Water from pump	30	-2331307	-1336	-9.21	366	0.36	0.00	0.04
Water to heat exchanger	31	-2330624	-1336	-9.12	366	0.36	0.00	0.04
Water to mixer 3	32	-683	-0.39	0.00	0.11	0.00	0.00	0.04
Water from heat exchanger	33	-2328785	-1330	-11.00	366	0.36	0.00	0.04

Table 3.2: Exergy table: atmospheric air and water

	$\dot{E}_{D(a)}$ **[kW]**	$\dot{E}_{D(b)}$ **[kW]**	ϵ_{abs} **[kW]**	ϵ_{rel} **[%]**
Compressor	27.24	27.25	0.01	0.05
Combustion chamber	1549.8	1552.4	2.58	0.17
Waste-heat boiler 1	945.3	945.3	0.02	0.00
Converter bed 1	46.0	41.2	4.86	10.6
Mixer 1	125.9	128.4	2.49	1.98
Converter bed 2	44.2	43.0	1.17	2.66
Mixer 2	37.8	39.7	1.84	4.86
Converter bed 3	5.84	5.52	0.32	5.47
Waste-heat boiler 2	164.4	164.5	0.08	0.05
Absorbtion column	491.4	443.7	47.63	9.69
Pump 1	3.28	0.14	3.14	95.9
Pump 2	0.00	0.00	0.00	-
Mixer 3	32.6	31.7	0.91	2.78
Acid cooler	234.6	234.1	0.54	0.23

Table 3.4: Exergy destruction table for all acid plant components, calculated by the entropy generation and by the exergy balance methods

	$\dot{W}$ **[kW]**
Compressor	98.592
Pump 1	0.218
Pump 2	1.471
Total pumps	1.689

Table 3.5: Work rates of the compressor and the pumps

	$\dot{E}_{D(a)}$ **[kW]**	$\mathbf{y}_D$ **[%]**	$\mathbf{y}^*_D$ **[%]**
Combustion chamber	1552	24.27	42.45
Waste-heat boiler 1	945	14.78	25.85
Absorbtion column	444	6.94	12.13
Acid cooler	234	3.66	6.40
Mixer 1	165	2.01	3.51
Waste-heat boiler 2	128	2.57	4.50
Converter bed 2	43.0	0.67	1.18
Converter bed 1	41.2	0.64	1.13
Mixer 2	39.7	0.62	1.08
Mixer 3	31.7	0.50	0.87
Compressor	27.3	0.43	0.75
Converter bed 3	5.52	0.09	0.15
Pump 1	0.14	0.00	0.00
Pump 2	0.00	0.00	0.00
Total	3657	57	100

Table 3.6: Exergy destruction rates for all acid plant components in order decreasingly, calculated by the entropy generation method.

Chapter 4

Economic Analysis

4.1 Introduction

In the first two chapters, the sulfuric acid production process of the reference plant was introduced and compared with another processes of the same kind, a flow sheet was presented, and the process was explained in detail. In the third chapter, a thermodynamic analysis in exergy terms was performed basically to know how exergy in our system is managed and which are the main points of exergy destruction and its locations. The current chapter evaluates the system economically, so later a connection between thermodynamics and economics could be done and finally a thermoeconomic analysis can be fulfilled. For that, in this chapter the *levelized* costs are presented.

There are different methods to approach an economic analysis. In the next sections, the *total revenue requirement method* (TRR method), which is based on procedures adopted by the Electric Power Research Institute (EPRI; 1993), is applied to perform an economic analysis in our process [5]. With this approach, the following steps have to be achieved:

- *First step.* Estimation of the total capital investment.
- *Second step.* Calculation of the total revenue requirement.
- *Third step.* Calculation of levelized costs.

In the first step, economic, financial, and plant operating parameters are assumed and all the costs associated with the project are calculated, including a minimum required return on investment. Once the total plant investment is estimated, in

the second step the annual revenue requirement is calculated using a *year-by-year analysis* and the results are summarized in a table. Finally, in the third step, levelized costs of the plant carrying charges, fuel costs, and operation and maintenance expenses are calculated, as well as the levelized cost of the main product; that is, the sale price of the sulfuric acid (78 wt%). Moreover, some economic principles as inflation, depreciation, and the cost of money will be reviewed, since they are required to complete these steps.

4.2 Estimation of the Total Capital Investment

The *total capital investment* (TCI) is an economic term which involves the sum of the *fixed-capital investment* (FCI) and *other outlays*. The fixed-capital investment consists on the capital needed to provide all the depreciable facilities such as purchased equipment, piping, instrumentation, etc. -excepting the costs associated with land, which is not depreciated- and it is divided into the costs which are always permanent in a plant, known as *direct costs* (DC), and the costs which momentarily remain during plant construction, known as *indirect costs* (IC). The direct costs can also be divided into two more classes by defining battery limits and auxiliary facilities. The boundary for battery limits includes all manufacturing equipment and its connections, but excludes administrative offices, storage areas, utilities, and other auxiliary facilities. In this thesis, we will refer to the investment inside the battery limits as *onsite costs* (ONSC), and *offsite costs* (OFSC) to the auxiliary facilities. The term *other outlays* refers to expenditures which cannot be classified neither as direct nor as indirect costs, but they are required for plant operation. There are four main other-outlays expenditures: *startup costs; working capital; costs of licensing, research, and development*; and *allowance for funds used during construction* (AFUDC).

For the estimation of TCI, the fixed-capital investment will be approached. For that, the purchased-equipment costs (PEC) must be determined, as explained in detail in the next Section 4.2.1. Once PEC is known, the remaining FCI costs are estimated through a *factor method*; that is, in terms of a percentage of PEC. For that, there is bibliography [5, 8, 11, 22, 23, 27], where different approaches for these percentages are given. It is important to pay attention and concentrate efforts es-

timating as realistic as possible PEC, since all plant fixed-capital investment and therefore the subsequent economic analysis strongly depend on that value. Figure 4.1 shows a division into categories of the TCI with its corresponding percentage ranges, averaged from bibliography [5]. It is noticed that the other-outlay expenditures are not calculated as PEC percentages. This and other aspects will be discussed in the next sections, including the complete definition of each item of the total capital investment.

1. Fixed-capital investment (FCI)
   (a) Direct costs (DC)
      i. Onsite costs (ONSC)
         - Purchased-equipment cost (PEC)
         - Purchased-equipment installation (20-90% of PEC)
         - Piping (50-70% of PEC)
         - Instrumentation and controls (6-40% of PEC)
         - Electrical equipment and materials (10-15% of PEC)
      ii. Offsite costs (OFSC)
         - Land (0-10% of PEC)
         - Civil, structural, and architectural work (20-33% of PEC)
         - Service facilities (30-100% of PEC)
   (b) Indirect costs (IC)
      i. Engineering and supervision (25-75% of PEC)
      ii. Construction costs including contractor's profit (15% of DC)
      iii. Contingencies (5-20% of FCI)
2. Other outlays
   (a) Startup costs (SUC) (5-12% of FCI)
   (b) Working capital (WC) (Section 4.2.4)
   (c) Allowance for funds used during construction (AFUDC) (Section 4.2.4)

Figure 4.1: Category division of the total capital investment (TCI)

4.2.1 Purchased-equipment costs

As explained before, to obtain an estimate of the capital cost of a chemical plant, the costs associated with major plant equipment (PEC) have to be known. For that, information such as materials of construction, size/capacity estimation from process conditions (Process Tables 2.3 and 2.4), and other data which define the main components of our plant should be collected in order to estimate purchase costs as realistic as possible. The accuracy of these costs relies on the amount and quality of the available information of its source. The most accurate estimate of the purchased cost of an equipment is provided by vendors' current price quotations. However, these quotations often are confidential information by means of keeping competence between vendors. The next best alternative is to use cost data from past purchase orders of same type components. Another technique is the use of estimating charts from literature, besides estimation software packages such as the java-script application offered by Matche Website (F.O.B. Golf Cost U.S.A.) [2], which gathers information from both current and past vendor quotations, and summary graphs.

In the estimate of purchased equipment, there are two principle estimation adjustments that have to be introduced: the *effect of capacity* and the *effect of time*.

The *effect of capacity* is used to estimate the purchase price of a desired component $C_{P,a}$ at capacity A_a, from the price of another component of the same type $C_{P,b}$ at capacity A_b by an exponential rule [Equation (4.1)].

$$C_{P,a} = C_{P,b}\left(\frac{A_a}{A_b}\right)^n \tag{4.1}$$

Capacity A_i corresponds to the design variable that defines the size of the i-equipment. For thermal systems, the exponent n is usually smaller than unity, since the percentage increase (or decrease) of the purchased cost is smaller than the percentage increase (or decrease) in equipment size. In the bibliography for this section, there are tables where escalating exponents for each type of thermal equipment are given. There is also a given size range, where the corresponding exponent is valid. In the absence of information, the *six-tenths rule* is used (exponent value of 0.6).

The *effect of time* represent the correction because of inflation that needs to be applied to costs from old price data. This correction basically actualizes past prices to a current or future year, known as *reference year*. This is done by using an appropriate *cost index* (CI). A number of different indices are used in the chemical

industry. In the present thesis, the *Chemical Engineering (CE) Plant Cost Index*, based on construction costs for chemical plants, is used. The reference is set in the middle of the year 2008. The following equation summarizes the explanation:

$$C_{P,2} = C_{P,1}\left(\frac{I_2}{I_1}\right) \tag{4.2}$$

where C_P and I represents purchase cost and cost index, respectively; Subscript 1 refers to base time when cost is known; and subscript 2 refers to time when cost is desired.

In the next subsections, it is estimated the purchase equipment cost of the following case study components: *compressor, heat exchangers, sulfur burner, converter*, and *absorber*. All costs are mostly calculated by using the Matche Website [2]. Process pumps are not considered, since the low power consumption (see Table 3.5) in such devices makes its purchase costs negligible in comparison with the other components.

Compressor

In the case study process, the compressor performs the function of blowing 16886 kg/h of atmospheric air (*stream 17*) to the sulfur burner, as well as increasing its inlet atmospheric pressure (1.013 bar) up to 1.2 bar (17.4 psi). For this component, CHEMCAD calculates a real power consumption of 98.59 kW (132.16 HP) (see Table 3.5). As explained in Section 1.2.3, a centrifugal compressor with its corresponding characteristics is purchased.

By Matche, the compressor cost estimate parameters are the following:

- Compressor type: Air, Centrifugal, 125 psi
- Compressor Power: 132.16 HP
- Material: Carbon Steel
- Cost 2007 US $: 71,000 ($C_{P,comp}$)

Two corrections have to be done to adjust the compressor purchased cost to thesis requirements. Initially, the price in dollars has to be converted into euros (mid-2007). Then, the cost in euros has to be brought to the reference year by means of inflation indexes (CE indexes).

$$C_{P,comp,2008} = C_{P,comp,2007} \times \text{Change } euros/dollars \text{ (2007)} \times \left(\frac{I_{CE,2008}}{I_{CE,2007}}\right) \tag{4.3}$$

$$C_{P,comp,2008} = 71,000 \times 0.748^{1} \times \left(\frac{554.8}{525.4}\right) = 56{,}097\ euros\ (mid - 2008) \tag{4.4}$$

Heat exchangers

In the plant, there are three heat exchangers: The first is situated between the sulfur burner and the contact group (*Heat exchanger 1* or *boiler 1*); the second, between the contact group and the absorber (*Heat exchanger 2* or *boiler 2*); and the third, in the absorbtion system (*Heat exchanger 3*).

Heat exchanger 1 corresponds to a heat-recovery boiler, which has the function of cooling the outlet SO_2 gases (*stream 2*) from the burner before they enter the first catalyst bed. In the heat exchanger, these gases have an inlet temperature of 1200 °C (T_2) and a required outlet temperature of 400 °C (T_3). CHEMCAD calculates a heat duty corresponding to this temperature difference of 3113.15 kW. The cooling heat is used to produce high pressure steam of 40 bar (580.15 psi). With this purpose, an evaporator of the type fire-tube is selected, where the hot gases flow through the pipes and the cooling water past the bundle. This type of evaporators have a heat transfer coefficient between 15 and 50 $\mathrm{Wm^{-2}K^{-1}}$ [3]. For the calculations a heat transfer coefficient of 40 $\mathrm{Wm^{-2}K^{-1}}$ is taken. Equations (4.5), (4.6), (4.7), and (4.8) show how the heat transfer area is calculated. The term *LMTD* corresponds to the *logarithmic mean temperature difference*.

$$\dot{Q} = k_1 A_1 LMTD \tag{4.5}$$

$$LMTD = \frac{(T_2 - T_{26}) - (T_3 - T_{25})}{\ln \frac{(T_2 - T_{26})}{(T_3 - T_{25})}} \tag{4.6}$$

$$3113.15 \times 10^3 = (40) A_1 \frac{(1200 - 250) - (400 - 100)}{\ln \frac{(1200 - 250)}{(400 - 100)}} \tag{4.7}$$

$$A_1 = 138\,\mathrm{m^2}\ (1485\,\mathrm{ft^2}) \tag{4.8}$$

By Matche, the heat exchanger 1 cost estimate parameters are the following:

- Exchanger Type: Evaporator, Horizontal Tube
- Area: 1485 $\mathrm{ft^2}$
- Material: Stainless Steel, 304

[1] June 2007, 1 dollar=0.748223 euros (http://www.x-rates.com)

- Internal Pressure: 600 psi, rating
- Cost 2007 US $: 778,100 ($C_{P,hx1}$)

By applying the same corrections as in Equation (4.3), the purchase cost of heat exchanger 1 is 614,770 euros (mid-2008).

Heat exchanger 2 corresponds also to a heat-recovery boiler of the same type as heat exchanger 1, with the function of cooling the converter outlet SO_3 gases (*stream 8*) with a temperature of 380 °C down to 120 °C. The heat duty is 1395.76 kW and high pressure steam of 5 bar (72.52 psi) is generated. Following the same procedure as in Equations (4.5), (4.6), (4.7), and (4.8), the heat transfer area has a surface of 408 m^2 (4393 ft^2). The calculations are performed with the same averaged heat transfer coefficient as with the first heat exchanger (40 $Wm^{-2}K^{-1}$).

By Matche, the heat exchanger 2 cost estimate parameters are the following:

- Exchanger Type: Evaporator, Horizontal Tube
- Area: 4393 ft^2
- Material: Stainless Steel, 304
- Internal Pressure: 150 psi, rating
- Cost 2007 US $: 1,097,900 ($C_{P,hx2}$)

The corrected price for heat exchanger 2 is 867,442 euros (mid-2008).

Heat exchanger 3 is located in the absorbtion system, concretely in the recirculation conduct. It is used for cooling 150155 kg/h of recirculating sulfuric acid (*stream 14*) from a temperature of 63.4 °C to 40 °C. Once the sulfuric acid is cooled, it enters the absorber. The heat duty is 1839.66 kW. Based on the information in Section 1.2.3, the heat exchanger selected is of the type shell-and-tube (800-1400 $Wm^{-2}K^{-1}$). The heat transfer area for a coefficient of 1100 $Wm^{-2}K^{-1}$ is 58 m^2 (620 ft^2).

By Matche, the heat exchanger 3 cost estimate parameters are the following:

- Exchanger Type: Shell/Tube, Fixed/U, Medium
- Area: 620 ft^2
- Material: Stainless Steel, 304
- Internal Pressure: 150 psi, rating
- Cost 2007 US $: 72,300 ($C_{P,hx3}$)

The corrected price for heat exchanger 3 is 57,124 euros (mid-2008). So the overall purchase equipment cost of the heat exchangers ($C_{P,hx1}$+$C_{P,hx2}$+$C_{P,hx3}$) yields 1,539,335 euros (mid-2008).

Sulfur Burner

The *sulfur burner* accomplishes the function of oxidizing the H_2S containing-gases (*stream 1*) with atmospheric air coming from the compressor (*stream 18*) in order to produce SO_2 (*stream 2*). The overall heat of reaction, calculated by CHEMCAD, is 4331.43 kW (14.78 million BTU/h). By Matche, the sulfur burner cost estimate parameters are the following:

- Incinerator Type: Direct Flame
- Duty: 14.78 million BTU/h
- Feed Material: Corrosive
- Cost 2007 US $: 313,900 ($C_{P,sburn}$)

The price of the sulfur burner after applying money conversion and effect of time correction is 248,010 euros (mid-2008).

Converter

The converter is a cylindrical vessel, composed of three catalyst beds which are cooled by air-quenching (bed1/bed2, bed2/bed3) where the sulfur dioxide-containing gases (*stream 3*) are oxidized into sulfur trioxide (*streams 4*, *6*, and *8*). Table 4.1 summarizes constructive specifications (L-longitude, D-diameter, V-volume). The catalyst masses have been calculated considering that the catalyst is of the type *O4-115 SR 10x5* (*Fill-density* ρ_B=469 kg/m^3 [24]).

	L [m]	**D [m]**	**V [L]**	**V [gallons]**	**Catalyst mass [kg]**
Catalyst bed 1	0.4	2.5	1963	519	921
Catalyst bed 2	10	2.5	49087	12968	23022
Catalyst bed 3	1	2.5	4909	1297	2302
Total			55960	14783	26245

Table 4.1: Contact group, size and mass specifications

The total volume of the converter is 55960 L (14783 gallons).

By Matche, the converter vessel cost estimate parameters are the following:

- Reactor Type: Jacketed, Non-Agitated
- Reactor Volume: 14783 gallons
- Material: Stainless Steel
- Internal Pressure: Atmospheric to 25 psi
- Cost 2007 US $: 131,200

The price of the converter vessel after applying money conversion and effect of time correction is 103,660 euros (2008). The total catalyst mass is 26,245 kg. So, taking into account an specific cost for O4-115 SR 10x5 catalysts of 15,000 euros/t (2007), the purchase cost of the catalysts is 393,676 euros (2008). Therefore, the total purchase price of the contact group ($C_{P,conv}$ = converter vessel + catalyst) is 497,336 euros (2008).

Absorber

The reference case distillation column consists of a vertical packed tower with the function of absorbing SO_3 containing-gas (*stream 9*) with liquid-phase H_2SO_4 (78 wt%) (*stream 15*). For determining the purchase cost of the tower, the design variable have to be known, in this case the *tower height (H_a)*. From bibliography [27], Equations (4.9), (4.10), and (4.11) are used to approach the tower height according with tower operating parameters. These parameters basically are: *number of stages (N)*, *gas flow velocity (v_g)*, and *gas flow volume rate ($\dot{V}_g$)* (*stream 9*). The values are the following:

- N=4 stages
- v_g=1.4 m/s (average of Section 1.2.3 given velocities)
- $\dot{V}_g$=3.77 m^3/s (stdV) (calculated by CHEMCAD)

$$H_a = N \times HETP \tag{4.9}$$

$$HETP = D^{0.3} \tag{4.10}$$

$$D = \left(\frac{4 v_g}{\pi \dot{V}_g} \right)^{0.5} \tag{4.11}$$

From Equation (4.11), it is calculated a column diameter of 1.85 m. Then, with

Equation (4.10), the height equivalent to a theoretical plate (HETP) is calculated with a value of 1.20 m. Finally, the total height of the column is estimated using Equation (4.9) with a value of 4.81 m, yielding a *tower volume* of 12.935 m^3.

The purchase cost of the absorber is approached by applying size corrections to the price of an absorber of 45.804 m^3 (D=1.80 m, H_a=18 m) made of Hastelloy. From bibliography, the purchase cost of the vessel and the packing correspond to 500,000 and 700,000 euros (mid-2008), respectively, so the sum is 1,200,000 euros (mid-2008). Applying Equation (4.1) with an escalating exponent of 0.6 [27], the following purchase tower cost is calculated:

$$C_{P,abs} = 1,200,000 \times \left(\frac{12.935}{45.804}\right)^{0.6} = 561{,}952\ euros\ (mid-2008) \tag{4.12}$$

Table 4.2 and Figure 4.2 summarize the Purchased Equipment Costs calculated in this section (rounded numbers):

	Purchase Cost [euros (2008)]	**Percentage [%]**
Compressor	56,100	1.9
Sulfur burner	248,010	8.5
Heat exchangers	1,539,330	53.0
Contact group	497,340	17.1
Absorber	561,940	19.4
TOTAL (PEC)	**2,902,720**	**100**

Table 4.2: Purchase Equipment Costs (PEC) (rounded values)

4.2.2 Direct Costs

Once PEC is known, the remaining direct costs can be estimated as a percentage of PEC (Figure 4.1). The costs presented in the following sections are rounded numbers.

Purchased-Equipment Installation

The installation implies the following costs: equipment transportation, costs for labor, foundations, and all other montage expenses related to the erection and nec-

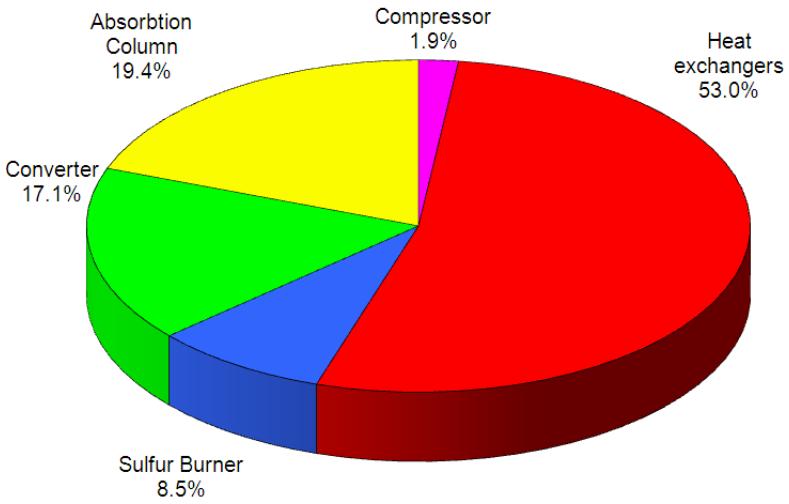


Figure 4.2: Purchase Equipment Costs (PEC) (%)

essary connections of the purchased equipment. Considering an economically favorable, unfavorable and intermediate case, the results are 580,544; 2,612,448; and 1,306,224 euros (mid-2008). The favorable and unfavorable cases are calculated by using the minimum and maximum percentages given in Figure 4.1, while the intermediate is calculated as the average of both cases. However, in other estimations, the intermediate case is calculated as a percentage recommended from bibliography to use in absence of information.

Piping

The piping costs in a chemical plant represent the material and montage costs required to complete the erection of all the piping used directly in the system. The piping of chemical plants handling fluids can be estimated in a range of 50-70%, with an average of 66% of purchased-equipment costs [5]. In the reference plant, this expenses present a value of 1,451,360; 2,031,904; and 1,915,795 euros (mid-2008).

Instrumentation and Controls

The percentage used to estimate these costs is higher as the degree of automation in the plant increases, while it is lower with an increasing plant total cost [5]. A range of 6-40% of purchased-equipment costs is usually used. In the absence of information, an average value of 20% should be taken. These costs imply expenses of 174,163; 1,161,088; and 580,544 euros (mid-2008).

Electrical Equipment and Materials

This is composed of the costs related to substations, distribution lines, switch gears, area lighting, etc. A range of 10-15%, with an average of 11%, is usually used to calculate these costs. The values are 290,272; 435,408; and 319,299 euros (mid-2008), respectively.

Land

This cost is determined by the location of the plant, and can be up to 10% of the purchased-equipment cost. In this thesis, land costs are estimated as 0 and 10% of PEC for limits cases, and 5% for the intermediate case. The values are 0; 290,272; and 145,136 euros (mid-2008), respectively.

Civil, Structural, and Architectural Work

These costs include the total cost for all buildings, including services, costs for roads, sidewalks, fencing, etc. The percentage of PEC used for this estimation depends on wether the plant refers to a new system at an new site or at an existing site. In this thesis, it refers to a new unit at an existing site, since the sulfuric acid plant is attached to a by-product plant from where the H_2S containing-flue gases are produced. For a new unit at an existing site, the percentage range and the average used are respectively 20-33% and 26.5%, with values of 580,544; 957,898; and 769,221 euros (mid-2008), respectively.

Service Facilities

This category implies all costs related with the supply of fuels, water, steam, and electricity (considering that these utilities are not generated in the main process), as well as environmental control, residual disposal, fire protection, first aid and facilities such as shops and cafeteria. The cost can be estimated in a range of 30-100%, with an average of 65% in absence of information. The values obtained are 870,816; 2,902,720; and 1,886,768 euros (mid-2008), respectively.

Accordingly, the sum of all direct costs presents limit values of 6,850,419; 13,294,458; and an average value of 9,825,707 euros (mid-2008).

4.2.3 Indirect Costs

Engineering and Supervision

Engineering and supervision includes all costs for developing the design of the plant: drawings, consultant fees and all costs related with cost engineering, scale models, engineering supervision, administration and travel. These costs are usually approached in a range of 25-75% (average 30%). The limit values are 725,680; 2,177,040; and the average 870,816 euros (mid-2008).

Including Contractor's Profit

The capital investment for these costs include all expenses during the construction of the plant. Temporary facilities, tools, equipment, personal located at the construction site, and the contractor's fee (profit) are included in this category. It is estimated with a 15% of the total DC: 1,027,563; 1,994,169 for limit cases; and 1,473,856 euros (mid-2008) for the average case.

Contingencies

Unpredictable events due to weather, work stoppages, sudden price changes, transportation difficulties, and design changes after completion of the design process can be contemplated with a factor ranging from 5 to 20% of the fixed-capital investment (FCI). The values obtained for limit cases and the average using a factor of 15% are 1,518,293; 3,082,176; and 2,147,714 euros (mid-2008), respectively.

The total indirect costs of the plant for limit cases are 3,271,536; 7,253,385; and for the average 4,492,386 euros (mid-2008). So, that yields a fixed-capital investment of 10,121,955; 20,547,843; and 14,318,093 euros (mid-2008).

4.2.4 Other Outlays

In this section, the following expenses are introduced: *startup costs; working capital; licensing, research, and development*; and *allowance for funds during construction (AFUDC)*. For that, Table 4.3 show parameters and assumptions that have to be taken into account. .

Parameter (units)	**Value**
Average nominal inflation rate (2008-2031) (%)	1.68[1]
Beginning of the design and construction period	1st of Jan., 2010
Date of commercial operation	1st of Jan., 2012
Plant economic life (years)	20
Capacity factor (%)	100
Labor positions for operating and maintenance	15[2]
Average labor rate (euros/h)	30[2]
Unit cost of fuel	
H_2S (euros/kg/h)	0[3]
Electricity (ct./kWh)	14.26[4] (2008)
Allocation of plant-facilities investment costs (%)	
1st of Jan. - 31th of Dec. 2010	40
1st of Jan. - 31th of Dec. 2011	60

Table 4.3: Economic and plant parameters

Startup Costs

These costs are related to expenses due to design changes after the plant construction but before operating. Labor, materials, equipment and all type of other expenses needed only during startup time are also included in this category, as well as the loss of income while the system is not operating at the desired capacity. Theses costs could be managed as one-time-only expenditure, but for the reference case they are capitalized; that is, they are part of the total capital investment, concretely part of the indirect costs. These costs are usually estimated in a range between 5 and 12% of FCI, being estimated in this thesis with percentages of 5 and 7% for limit cases, and 6% for the intermediate case. This category represents expenses of 506,098; 1,438,349; and 859,086 euros (mid-2008), respectively.

[1] Average of the last five annual inflation rates (consumer prices) in Germany [1].

[2] Value taken from bibliography

[3] The fuel (H_2S) presents cost zero, since it is a flue gas from a by-product plant.

[4] http://www.vattenfall.de (Geschäftskunden/Stromprodukte bis 100000 kWh/Berlin Profi)

Working Capital

During plant operation, fuel and maintenance costs associated to one year are expected to be payed with the annual revenue. The *working capital* (WC) represents the funds needed to cover these costs before payments are received through the sale of plant products. Therefore, it depends on the average length of time that a product needs to be manufactured and reach the costumer, besides the time it takes to receive payment for the product sold. The working capital includes the money invested in raw materials, fuels, and supplies carried in stock, finished products in stock and semifinished products being manufactured, accounts receivable, cash kept on hand for operating expenses, taxes, and other current obligations, and accounts payable.

Before the calculation of the WC, two terms have to be calculated: the *fixed* and *variable operating and maintenance costs*. These costs are calculated as the double and the 20% of *direct personal costs* (or labor costs), respectively. In order to calculate labor costs, it is considered in this work that a labor works 8 hours per day, five days per weak, and 48 weeks per year. Consequently, one labor works 1,920 annual hours. That yields 864,000 euros (mid-2008) of direct personal costs [Equation (4.13)]. The sum of fixed and variable operating and maintenance costs is known as the *total annual operating and maintenance costs* (OAM), that even though it is not taken into account in the calculation of the WC, it will be used in next sections. All results are showed in Table 4.5.

$$15\,\text{workers} \times \frac{30\,\text{euros}}{1\,\text{hour}} \times \frac{1920\,\text{h}}{1\,\text{year}} = 864,000\,\text{euros}\ (mid-2008) \tag{4.13}$$

	euros (mid-2008)
Direct personal costs	864,000
Fixed annual operating and maintenance costs (2×DC)	1.728,000
Variable annual operating and maintenance costs (0.2×DC)	172,800
Total annual operating and maintenance costs (OAM)	**1.900,800**

Table 4.4: Annual operating and maintenance costs

From bibliography, the working capital can be calculated as the sum of the

following expenses:

- (a) 2 months of fuel plus variable operating and maintenance costs at full load [Equation (4.14)].
- (b) 3 months of direct personal costs [Equation (4.15)].
- (c) a contingency of 25% of the total of the above three items.

It should be remarked that the term (a) corresponds to two months of the annual variable costs from Table 4.4, since the plant always works at full load and the fuel cost is zero (see Table 4.3). The WC results are summarized in table 4.5.

$$172,800\,\text{euros} \times \frac{1\,\text{year}}{12\,\text{months}} \times 2\,\text{months} = 28,800\,\text{euros}\ (mid-2008) \tag{4.14}$$

$$864,000\,\text{euros} \times \frac{1\,\text{year}}{12\,\text{months}} \times 3\,\text{months} = 216,000\,\text{euros}\ (mid-2008) \tag{4.15}$$

	euros (mid-2008)
(a)	28,800
(b)	216,000
(c)	61,200
Working capital	**306,000**

Table 4.5: Working capital and associated costs

Allowance for Funds During Construction (AFUDC)

During the time between the beginning of construction (1st of January, 2010) and system startup (1st of January, 2012), parts of the investment have to be released in order of paying (a) the cost of land, (b) the plant-facilities investment (PFI), and (c) startup costs. The *plant-facilities investment* represents the fixed-capital investment minus land costs. The *allowance for funds during construction* consists of the interests that have to be paid during this period due to a plan of financing (Table 4.6). The financing can be fulfilled by means of company resources and direct loans, according to an interest rate equal to the *weighted cost of capital* (cost of money). The interest is accounted on an annual basis (end of year) during the

construction period for all funds spent during the year or previous years. In this work, the annual basis is the last year of construction period (2011), so all interests are calculated . Table 4.7 shows time assumptions for plant costs; that is, the date at which expenses have to be escalated using Equations (4.16) and (4.17), which are introduced later. It should be remarked that the working capital does not generate interests accounted in the AFUDC during the construction period, since WC occurs at end of that period (see Table 4.7).

Type of financing	Common Equity	Preferred Stock	Debt
Financing fraction (%)	35.0	15.0	50.0
Required annual return (%)	15.0	11.7	10.0
Resulting average cost of money (%)			12.0

Table 4.6: Plan financing fractions and required returns on capital

Expense concept	**Release date**
Land	1st of Jan., 2010
40% of PFI	1st of July, 2010
60% of PFI	1st of July, 2011
Startup costs	1st of July, 2011
AFUDC	31st of Dec., 2011
Working capital	31st of Dec., 2011

Table 4.7: Release dates for plant expenses [5]

For calculating AFUDC, it is necessary to introduce the *time value of money* concept. This concept relies on that an euro in hand today is worth more than an euro one year later. That happens because of the fact that the euro in hand can be invested for the year. This principle is useful in a cost evaluation, since it enables to compare amounts of money over the time. There are two basic formulas deriving from this concept:

1. **Present Value**. Equation (4.16) calculates the *future value, F*, of a present amount, P, deposited in an account at a given effective *interest rate,* i_{eff}, which

is compounded at the end of each of n time periods. In this equation, this term is a percent also known as *rate of return*, or *annual cost of money*. The term *rate of return* refers to an investment made, while the term *annual cost of money* refers to the rate at which the use of borrowed money is compounded, for example when calculating AFUDC at the year at which this expense has to be released (see Table 4.7).

$$F = P(1 + i_{eff})^n \tag{4.16}$$

2. **Future Value**. Equation (4.17) is useful to know the present value, P, of an economic operation that will be payed in the future at an amount F. The term i_{eff} is known as effective *discount rate*. For example when calculating AFUDC at the year at which the plant economic analysis is estimated (middle of 2008).

$$P = F\frac{1}{(1 + i_{eff})^n} \tag{4.17}$$

The calculation of AFUDC is summarized in Table 4.8 for the three possible cases. This table basically shows how the expenses (a), (b), and (c) are distributed into the different types of financing at their date of release (Escalated investment columns for the PFI and in parenthesis for land and startup costs); as well as its corresponding compounded interest (AFUDC columns). For the escalation of the expenses it is used as effective interest rate the annual inflation rate from Table 4.3. Therefore, the sum of the total AFUDC of each type of financing corresponds to the total escalated AFUDC (end-2011). Now, in terms of calculating the TCI of the plant (mid-2008 euros), the escalated AFUDC has to be brought to the year at which the economic analysis is estimated as explained before; that is mid-2008. For that, it is used Equation (4.17) with the total AFUDC at end-2011 euros as future value, F, and the cost of money (see Table 4.6) as effective discount rate, i_{eff}. The calculations shown by Equations (4.18) and (4.19), in rounded values and in thousand of euros, correspond only to the intermediate case. The AFUDC for the other cases can be found in Tables 4.9 and 4.10.

$$\text{Total } AFUDC = 745 + 248 + 706 = 1{,}699 \,\text{euros } (end - 2011) \tag{4.18}$$

$$P = 1{,}699\frac{1}{(1 + 0.12)^{3.5}} = 1{,}143 \,\text{euros } (mid - 2008) \tag{4.19}$$

	Plant-Facilities Investment		Common Equity		Preferred Equity		Debt	
Calendar Year	Mid-2008 keuros	Escalated Investment	Escalated Investment	AFUDC	Escalated Investment	AFUDC	Escalated Investment	AFUDC
2010	4,049	4,186	1,465	342	628	113	2,093	322
2011	6,073	6,384	2,235	162	958	54	3,192	156
Subtotals[1]	10,122	10,570	3,700	503	1,586	168	5,285	477
		(A)	(B)	(C)	(D)	(E)	(F)	(G)
AFUDC for the cost of land (0 euros expended on 1st of Jan., 2010)			0	0	0	0	0	0
AFUDC for startup costs (532 euros expended on 1st of July, 2011)			186	13	80	4	266	13
Totals (Favorable)				**517**		**172**		**490**
2010	5,669	5,861	2,051	478	879	159	2,931	450
2011	8,504	8,940	3,129	226	1,341	76	4,470	218
Subtotals[1]	14,173	14,801	5,180	705	2,220	235	7,400	669
AFUDC for the cost of land 149 euros expended on 1st of Jan., 2010)			52	17	22	6	74	16
AFUDC for startup costs (903 euros expended on 1st of July, 2011)			316	23	135	8	452	22
Totals (Intermediate)				**745**		**248**		**706**
2010	8,103	8,378	2,932	684	1,257	227	4,189	644
2011	12,155	12,777	4,472	324	1,917	109	6,389	312
Subtotals	20,258	21,155	7,404	1,008	3,173	336	10,578	956
AFUDC for the cost of land (298 euros expended on 1st of Jan., 2010)			104	34	45	11	149	31
AFUDC for startup costs (1,512 euros expended on 1st of July, 2011)			529	38	227	13	756	37
Totals (Unfavorable)				**1,079**		**360**		**1,024**

Table 4.8: Calculation of AFUDC (end-2011 values) (all values are rounded and given in thousands of euros)

[1](A)=(B)+(D)+(F); (B)=0.35(A); (D)=0.15(A); (F)=0.55(A)

Table 4.9 shows a summary of terms (escalated euros) in order of calculating the *total net outlay*, *total AFUDC*, *total capital investment*, *total capital nondepreciable investment*, and the *total capital depreciable investment*. The third term refers to all expenses needed to build the plant (Land and PFI) and to start working (SUC and WC), while the fourth and the fifth show how these expenses are payed. The fourth term refers to those expenses that are not payed gradually, but as one-time expenditure. Concretely, they are payed at the end of the plant economic life (end-2031). On the contrary, the fifth term refers to those expenses that are payed along the plant working period (2012-2031). It should be remarked that the value of the third term does not correspond to the value of the TCI shown in Table 4.10, since this last value is expressed in mid-2008 euros and the other in escalated euros. Consequently, the TCI is allocated in an interval of [11,727; 23,949], with an intermediate value of 16,626 rounded thousand euros (mid-2008), which is closer to the favorable case than to the unfavorable case.

In terms of validating the cost estimation for the TCI, it can be used the *Lang factor*. This factor estimates the total capital investment of a chemical plant by means of the PEC [Equation (4.20)]. According to the type of plant, it adopts different values. In this thesis, a Lang factor of 4.74 is taken since the case study plant is considered as a fluid processing plant [27]. Thus, the TCI estimated by this factor presents a value of 13,759 of rounded thousand euros (mid-2008). This result is allocated between the favorable and intermediate case of this thesis.

$$\begin{aligned} TCI &= F_{Lang} \cdot PEC \qquad (4.20) \\ TCI &= 4.74 \cdot 2,903 = 13{,}759\,\text{euros}\ (mid-2008) \end{aligned}$$

4.3 Calculation of the Total Revenue Requirement

The annual *total revenue requirement (TRR)* for a plant is the revenue that has to be collected annually by means of selling all products to compensate all expenditures incurred in the same year and to ensure economic profit. The total revenue requirement is composed of two main categories: *carrying charges* and *expenses*.

The first category includes all costs that are capitalized, that is the obligations

	Favorable	Intermediate	Unfavorable
Cost of land (1/1/2010)	0	149	298
Escalated PFI from Table 4.8 (30/6/10 and 30/6/11)	10,570	14,801	21,155
Startup costs (30/6/11)	532	903	1,512
Working capital (31/12/11)	324	324	324
Total net outlay	11,426	16,177	23,289
Common equity AFUDC	517	745	1,079
Preferred equity AFUDC	172	248	360
Debt AFUDC	490	706	1,024
Total AFUDC	1,180	1,699	2,463
Total net outlay	11,426	16,177	23,289
Total AFUDC	1,180	1,699	2,463
Total capital investment	12,607	17,876	25,752
Cost of land (1/1/2008)	0	149	298
Working capital (31/12/11)	324	324	324
Common equity AFUDC	517	745	1,079
Total nondepreciable capital investment	841	1,218	1,701
Total capital investment	12,607	17,876	25,752
Total nondepreciable capital investment	(-)841	(-)1,218	(-)1,701
Total depreciable capital investment	11,765	16,658	24,051

Table 4.9: Total capital investment and related costs I (all costs are rounded and expressed in thousands of escalated euros)

that remain until the end of the plant economic life: *capital recovery, return on equity*, and *return on debt*. Additionally, it is defined the *minimum acceptable return (MAR)* as the minimum return on investment that the company expects from the project (return on equity plus return on debt). The second category includes the expenses that are payed with the revenue and for that reason, they are not capitalized. These expenses are: *fuel costs* and *operating and maintenance costs*. Since the hydrogen sulfide-gases present zero cost (Table 4.3), the fuel expenses are basically related to the electric consumption of the plant; that is, the power of the compressor

	Favorable	Intermediate	Unfavorable
Purchased-equipment cost (PEC)	2,903	2,903	2,903
Purchased-equipment installation	581	1,306	2,612
Piping	1,451	1,916	2,032
Instrumentation and controls	174	581	1,161
Electrical equipment and materials	290	319	435
Onsite costs (ONSC)	5,399	7,025	9,144
Land	0	145	290
Civil, structural, and architectural work	581	769	958
Service facilities	871	1,887	2,903
Offsite costs (OFSC)	1,451	2,801	4,151
Direct costs (DC)	6,850	9,826	13,294
Engineering and supervision	726	871	2,177
Construction costs including contractor's profit	1,028	1,474	1,994
Contingencies	1,518	2,148	3,082
Indirect costs (IC)	3,272	4,492	7,253
Fixed-capital investment (FCI)	10,122	14,318	20,548
Startup costs (SUC)	506	859	1,438
Working capital (WC)	306	306	306
Allowance for funds used during construction (AFUDC)	793	1,143	1,656
Other outlays	1,605	2,308	3,401
Total capital investment (TCI)	**11,727**	**16,626**	**23,949**

Table 4.10: Total capital investment and related costs II (all costs are rounded and expressed in thousands of mid-2008 euros)

and the pumps. For paying the TRR, it is assumed that the revenues from the sale of products are received in the middle of each year during the system's economic life. The costs for operation and maintenance (OAM) are also allocated in the middle of each year.

The total revenue requirement for the jth year, TRR_j, corresponds to the sum of all above annual amounts:

$$TRR_j = TCR_j + ROI_{j,ce} + ROI_{j,ps} + ROI_{j,d} + OAM_j + FC_j \tag{4.21}$$

where TCR is the total capital recovery; ROI is the minimum return on investment for common equity (subscript ce), preferred stock (subscript ps), and debt (subscript d); OAM are the operation and maintenance costs; and FC are the fuel costs. The

OAM costs are calculated in Table 4.4 initially in the year 2008, so each year they have to be recalculated due to the inflation rate. The fuel costs are calculated in Equation (4.22) by multiplying the electric power of the compressor and the pumps (Table 3.5) by the annual working hours of the plant.

$$\begin{aligned} FC_{2008} &= (98.59 + 1.69)\,\text{kW} \times \frac{8760\,\text{hours}}{1\,\text{year}} \times \frac{0.1426\,\text{euros}}{1\,\text{kWh}} = \\ &= 125,269\,\text{euros}\ (mid - 2008) \end{aligned} \tag{4.22}$$

The **total capital recovery** of the jth year is composed of two annual amounts [Equation (4.23)]: the annual *book depreciation (BD)* and the annual *recovery of common equity (RCEAF)*. The annual book depreciation is calculated by the *straight-line* method [Equation (4.24)]:

$$TCR_j = BD_j + RCEAF_j, \quad j = 1, ..., BL \tag{4.23}$$

$$BD_j = \frac{TDI}{BL}, \quad j = 1, ..., BL \tag{4.24}$$

where BD is the annual *book depreciation* in the jth year, TDI the *total depreciable investment* (see Table 4.9), and BL the *book life* (20 operating years). For the limit cases and the intermediate case the rounded values are 588; 1,203; and 833 thousand of euros (beginning of 2012), respectively. It should be remarked that the cost of land and the working capital are not included in the total capital recovery, since they are returned at the end of the economic life (end-2031) as a one-time-only expenditure.

The common-equity allowance for funds used during construction (AFUDC_{CE}) (see Table 4.9) has to be recovered, since it is not included in the depreciable capital investment. For that, it is used a constant annual amount (RCEAF) [Equation (4.25)].

$$RCEAF_j = \frac{AFUDC_{CE}}{BL}, j = 1, ..., BL \tag{4.25}$$

For the limit cases and the intermediate case the rounded values are 26, 54, and 37 thousand of euros (beginning of 2012), respectively. That yields a TCR of 614; 1,257; and 870 thousand of euros.

Returns on equity and debt. The interests generated by equity and debt during the plant construction period are returned by means of the total capital recovery.

However, during plant operation, equity and debt still generate interests because of plant recovery. Theses interests are calculated annually by multiplying the amount of money that still has to be payed at the beginning of the year (BBY) with the corresponding required annual return (see Table 4.6). Equation (4.26) calculates the ROI for the year j and for the type of financing i_x (x=*ce*, *ps*, and *d*).

$$ROI_{j,x} = BBY_j \cdot i_x \tag{4.26}$$

Table 4.11 shows a year-by-year schedule with all interests generated by each financing category for the intermediate case. The term BBY means *balance at the beginning of the year*, so the BBY_{2012} for each type of financing consists of the pondered values of TCI (value from Table 4.9) using the respectively financing fractions (Table 4.6). Then, the next balance, BBY_{2013}, presents the value of BBY_{2012} minus the book depreciation -in the case of the common equity minus the RCEAF, as well- that at the end of each year has to be payed. At the end of the year 2031, the BBY corresponds to the value of land plus the WC. In Appendix A.1, the schedules for the two remaining cases can be found.

Once the TCR and the ROI are known, it is possible to calculate the total revenue requirement for each year. For that, as explained in before, it is assumed that both operation and maintenance, and fuel costs become more expensive each year with the inflation rate of Table 4.3. In the case of OAM-costs, they were calculated in the WC section in mid-2008 euros (see Table 4.4), so they have to be escalated using Equation (4.17) into mid-2012 euros, since at the middle of 2012 is the first paying date for such expenses. Therefore, it yields 2,032 of rounded thousand euros (mid-2012). On the other hand, the fuel costs are calculated with Equation (4.22) in the middle of the year 2008, but no escalation with the inflation rate to the year 2012 is needed, since the price of electricity per kilowatt-hour (see Table 4.3) is taken as a constant until the end of the first year of plant operation (2012). From the year 2013 on, fuel costs increase annually by means of the inflation rate. Table 4.12 shows all values of the TRR for the intermediate case during plant operation. Same information for the other cases can be found in the Appendix A.2.

	Common Equity				Preferred Stock			Debt		
Year	BBY	BD	RCEAF	ROI	BBY	BD	ROI	BBY	BD	ROI
2012	6,257	252	37	939	2,681	134	314	8,938	447	894
2013	5,968	252	37	895	2,547	134	298	8,491	447	849
2014	5,678	252	37	852	2,413	134	282	8,044	447	804
2015	5,389	252	37	808	2,279	134	267	7,597	447	760
2016	5,100	252	37	765	2,145	134	251	7,151	447	715
2017	4,811	252	37	722	2,011	134	235	6,704	447	670
2018	4,522	252	37	678	1,877	134	220	6,257	447	626
2019	4,232	252	37	635	1,743	134	204	5,810	447	581
2020	3,943	252	37	591	1,609	134	188	5,363	447	536
2021	3,654	252	37	548	1,475	134	173	4,916	447	492
2022	3,365	252	37	505	1,341	134	157	4,469	447	447
2023	3,076	252	37	461	1,207	134	141	4,022	447	402
2024	2,787	252	37	418	1,073	134	125	3,575	447	358
2025	2,497	252	37	375	939	134	110	3,128	447	313
2026	2,208	252	37	331	804	134	94	2,681	447	268
2027	1,919	252	37	288	670	134	78	2,235	447	223
2028	1,630	252	37	244	536	134	63	1,788	447	179
2029	1,341	252	37	201	402	134	47	1,341	447	134
2030	1,052	252	37	158	268	134	31	894	447	89
2031	762	252	37	114	134	134	16	447	447	45
end-2031	473	-	-	-	0	-	-	0	-	-

Table 4.11: Year-by-year distribution of capital recovery and interests generated during plant operation (ROI) (all costs are rounded and expressed in thousands of escalated euros)

4.4 Levelized costs

In the last section, the total revenue requirement (TRR) was calculated as a varying annual amount, as well as the operating and maintenance and fuel costs due to inflation and the financing plan interest rates. Nevertheless, varying amounts are

Year	TCR	ROI_{ce}	ROI_{ps}	ROI_{d}	OAM	FC	TRR_{cu}	TRR_{ct}
2012	870	939	314	894	2,032	125	5,173	4,619
2013	870	895	298	849	2,066	127	5,106	4,070
2014	870	852	282	804	2,101	130	5,039	3,586
2015	870	808	267	760	2,136	132	4,973	3,160
2016	870	765	251	715	2,172	134	4,907	2,784
2017	870	722	235	670	2,208	136	4,842	2,452
2018	870	678	220	626	2,245	138	4,778	2,160
2019	870	635	204	581	2,283	141	4,714	1,903
2020	870	591	188	536	2,321	143	4,651	1,676
2021	870	548	173	492	2,360	146	4,588	1,477
2022	870	505	157	447	2,400	148	4,527	1,301
2023	870	461	141	402	2,440	150	4,466	1,146
2024	870	418	125	358	2,481	153	4,406	1,009
2025	870	375	110	313	2,523	156	4,346	889
2026	870	331	94	268	2,566	158	4,287	783
2027	870	288	78	223	2,609	161	4,229	689
2028	870	244	63	179	2,652	164	4,172	607
2029	870	201	47	134	2,697	166	4,116	535
2030	870	158	31	89	2,742	169	4,060	471
2031	870	114	16	45	2,788	172	4,005	415

Table 4.12: Year-by-year revenue requirement analysis for the medium case (all costs are rounded and expressed in thousands of mid-2008 euros). The terms TRR_{cu} and TRR_{ct} correspond with the escalated values and the values brought to the middle of the year 2011 of the total revenue requirement, respectively.

not suitable for evaluating the cost effectiveness and considering design modifications of a thermal system, but levelized costs.

In this section, the *levelized total required revenue* (TRR_L), the *levelized operation and maintenance costs* (OAM_L), and the *levelized fuel costs* (FC_L) are calculated, so the *levelized carrying charges* (CC_L) and the levelized selling price of the sulfuric acid can be determined, also known as the *main-product unit cost* (MPUC). These

results are required to perform a thermoeconomic analysis (Chapter 5), which differs from a conventional economic analysis in the fact that the first is done at the plant component level. For the calculation of the levelized costs, it has to be introduced the *capital recovery factor* and the economical concept of *levelization*:

1. **Capital recovery factor** (CRF). Given an amount of P, it can be levelized into equal amounts A that are payed at the end of each year along n years, at a rate of return (cost of money) i_{eff} as shown in Equation (4.27).
2. **Levelization**. Given an amount of P_o present euros, which each year becomes more expensive because of a nominal inflation rate, r_n, it can be levelized into equal amounts A that are payed at the end of each year along n years, at a rate of return (cost of money) i_{eff} using the *CELF factor* (constant-escalation levelization factor) shown in Equation (4.28). Additionally, it should be remarked that the term levelization is also used in this thesis as a shortened form to say that an expense is distributed uniformly along a number of time periods.

$$A = CRF \cdot P = \frac{i_{eff}(1+i_{eff})^n}{(1+i_{eff})^n - 1} \cdot P \tag{4.27}$$

$$A = CELF \cdot P_o = \frac{k(1-k^n)}{1-k} \cdot P_o \tag{4.28}$$

$$k = \frac{1+r_n}{1+i_{eff}} \tag{4.29}$$

Once both CRF and CELF factors are introduced, the levelized costs can be calculated. For the calculation of the levelized total required revenue, the CRF factor is applied, so a present amount P by means of the annual TRR has to be calculated. For that, all annual TRR amounts have to be brought to the middle of the year 2011 by using the cost of money as discount rate (TRR_{ct}-values from Table 4.12) and then, they are summed yielding P. The reason why the present value P is set in the middle of the year 2011 and not at the beginning of 2012 is due to the CRF-formula [Equation (4.27)], which distributes the levelized TRR values at the end of each year. This fact can be understood easier by examining Figure 4.3. The P-values are 30,641; 43,964; and 35,731 thousand of rounded euros for the favorable, unfavorable, and intermediate case, respectively. By multiplying these values with a capital recovery factor of 0.134, the following TRR_L values are obtained:

4,103; 5,888; and 4,785. The calculations are shown for the intermediate case in the equations above.

$$CRF = \frac{0.1201(1+0.1201)^{20}}{(1+0.1201)^{20}-1} = 0.134 \;\; (rounded\ value) \tag{4.30}$$

$$TRR_L = 0.134 \times 35,731,200\,\text{euros} = 4,785,150\,\text{euros} \tag{4.31}$$

For the calculation of the levelized operation and maintenance costs, the value shown in Table 4.4 has to be brought to the first year of paying (mid-2012) using the inflation rate shown in Table 4.3. Then, the levelized cost is calculated by using a CELF factor of 1.128 [Equation (4.34)]. That yields 2,292 thousand of rounded euros. The calculations are shown in the equations above.

$$1,900,800\,\text{euros} \times (1+0.0168)^4 = 2,031,789\,\text{euros} \tag{4.32}$$

$$k = \frac{1+0.0168}{1+0.1201} = 0.908 \tag{4.33}$$

$$CELF = \frac{0.908(1-0.908^{20})}{1-0.908} = 1.128 \;\; (rounde\ value) \tag{4.34}$$

$$OAM_L = 1.128 \times 2,031,789\,\text{euros} = 2,292,324\,\text{euros} \tag{4.35}$$

For the fuel costs, the same procedure is performed -the same CELF factor as for the OAM-costs is used- yielding a levelized value of 141,332 euros [Equation (4.36)]. The levelized price of electricity per kilowatt-hour is calculated for the thermoeconomic analysis (Section 5) in Equation (4.37).

$$FC_L = 1.128 \times 125,269\,\text{euros} = 141,332\,\text{euros} \tag{4.36}$$

$$\begin{aligned} c_{W,L} &= \frac{FC_L}{(\dot{W}_{comp}+\dot{W}_{pumps}) \times 8760\,\text{h/year}} = \\ &= \frac{141,332\,\text{euros}}{(98.59+1.689)\times 8760} = 16.09\,\text{ct./kWh} \end{aligned} \tag{4.37}$$

The levelized carrying charges can be calculated now by subtracting the levelized costs for operation and maintenance from the levelized total required revenue. Thus, the results for the favorable, unfavorable, and intermediate case are 1,670; 3,454; and 2,351 thousand of rounded euros, respectively. The calculations for the intermediate case are shown in the equations above.

$$CC_L = TRR_L - OAM_L - FC_L \tag{4.38}$$

$$CC_L = 4,785,150 - 2,292,324 - 141,332\,\text{euros} = 2,351,494\,\text{euros} \tag{4.39}$$

Then, the main-product unit cost can be calculated with Equation (4.44), assuming a selling price for the plant by-products; that is, steam at 40 and 5 bar. From bibliography [5], it is found that the sale price of vapor at 40 bar presents an approximated value of 0.035 dollars/kg (mid-1996) 20-year levelized, so the sale price of vapor per unit of exergy can be calculated in order to determine the sale price at any vapor pressure. The procedure is the following: first, the sale price of vapor at 40 bar is converted into euros (mid-1996) using historical dollar-euro indexes; second, the result is converted into euros (mid-2008) by means of CE indexes; third, the price of vapor per exergy is calculated with Equation (4.41). The specific exergy for the vapor steam at 40 bar is taken from Table 3.2.

$$0.035\,\text{dollars/kg}\,(mid-1998) \times 0.9174\ \text{euros/dollar}^1\,(mid-1998) \times \times \left(\frac{554.8}{389.5}\right) = 0.046\,\text{euros/kg}\,(mid-2008) \tag{4.40}$$

$$\frac{0.046\,\text{euros/kg}\,(mid-2008)}{1.01\,\text{MJ/kg}} \times \frac{3.6\,\text{MJ}}{1\,\text{kWh}} = 0.164\,\text{euros/kWh}\,(mid-2008) \tag{4.41}$$

The so-called *by-products value* (BPV) that appears in Equation (4.44) consists of the levelized revenue from selling the steam produced in one operating year. This value is calculated simply by multiplying the selling price of the steam per exergy with its annual production (*process streams 26* and *28*). That yields a levelized steam revenue of 2,520,565 euros/year [see Equation (4.42)].

$$BPV = 0.164\ \text{euros/kWh} \times (1,315 + 443\,\text{kW}) \times \times \frac{8,760\,\text{h}}{1\,\text{year}} = 2,520,565\ \text{euros/year} \tag{4.42}$$

The term MPQ of Equation (4.44) is called the *main-product quantity* and consists of the annual production of sulfuric acid (*process streams 12*) with a value of 22,604 t [see Equation (4.43)]. Therefore, the levelized selling-price of the sulfuric acid corresponds to 6.9, 14.7, and 10.0 ct./kg (euro) for the favorable, unfavorable, and intermediate case, respectively. In comparison with the average values published by the *Chemical Market Reporter (January-April 2001)*, the price of the sulfuric acid in 2001 has a value of 4.8 ct./kg (dollar), that approximately corresponds to

[1] July 1998, 1 dollar=0.9174 euros (http://www.x-rates.com)

7.3 ct./kg (euro) in 2008 [Equation (4.47)]. That shows that both reported and estimated price have the same order of magnitude. The calculations for the intermediate case are shown by Equation (4.45).

$$MPQ = 2580\,\text{kg/h} \times \frac{8,760\,\text{h}}{1\,\text{year}} = 22,602,447\,\text{kg/year} \tag{4.43}$$

$$MPUC = \frac{TRR_L - BPV}{MPQ} \tag{4.44}$$

$$MPUC = \frac{4,785,149 - 2,520,565}{22,602,447} = 0.1002\,\text{euros/kg} \tag{4.45}$$

$$= 10.02\,\text{ct./kg} \tag{4.46}$$

$$4.8\,\text{ct./kg (dollar)}\,(Feb.\,2001) \times 1.0855\ \text{euros/dollar}^2\,(Feb.\,2001) \times \times \left(\frac{554.8}{394.3}\right) = 7.3\,\text{ct./kg (euro)}\,(mid - 2008) \tag{4.47}$$

[2]February 2001, 1 dollar=1.0855 euros (http://www.x-rates.com)

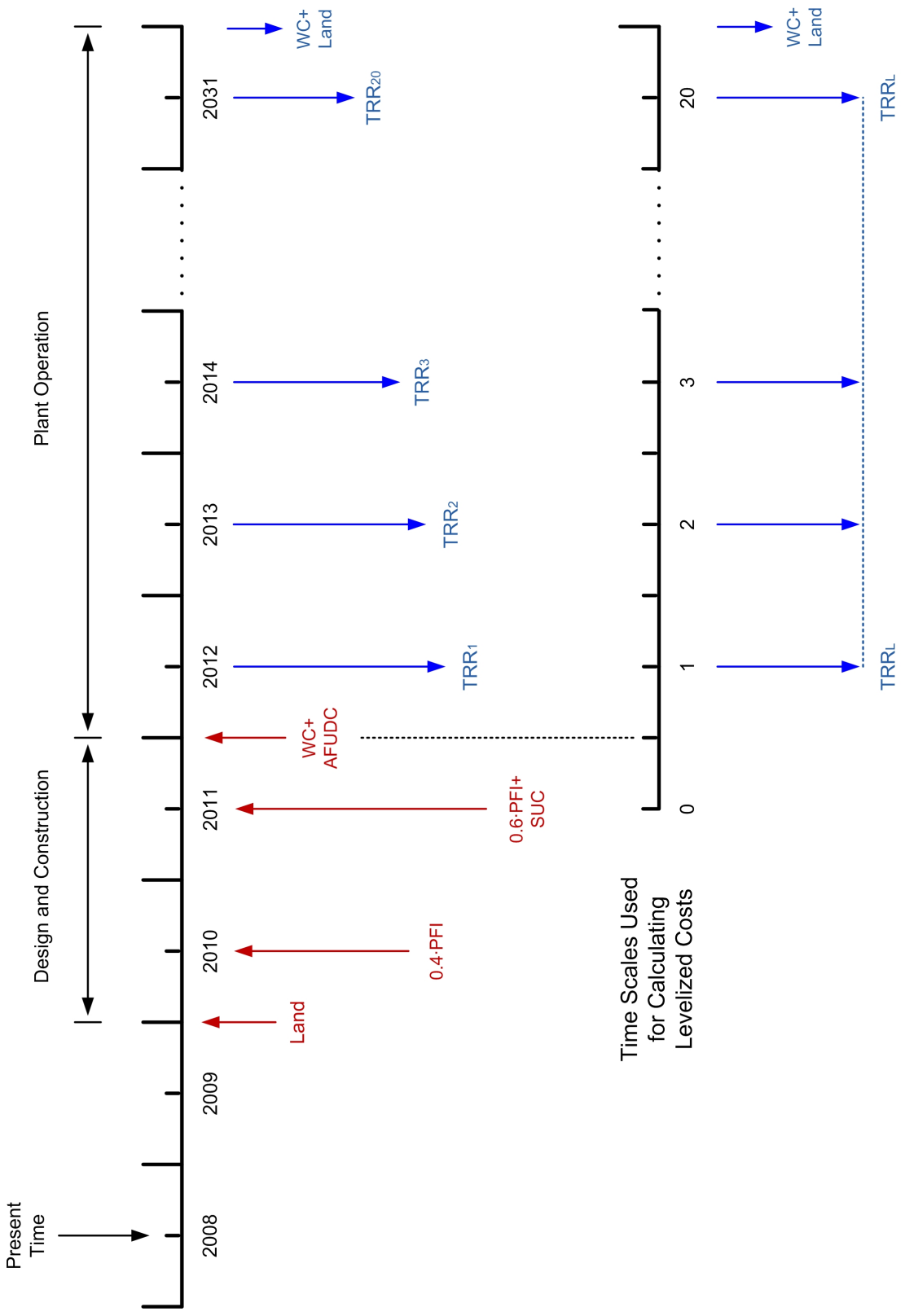


Figure 4.3: Time Scales

Chapter 5

Thermoeconomic Analysis

This chapter combines the exergy analysis with the economic analysis presented in Chapters 3 and 4, respectively. Here, the basic elements of thermoeconomics are discussed: cost balances, means for costing exergy transfers, and thermoeconomic variables used to evaluate and later optimize a thermal or chemical system.

As defined in [5], *thermoeconomics is the branch of engineering that combines exergy analysis and economic principles to provide the system designer or operator with information not available through conventional exergy analysis and economic evaluations but crucial to the design and operation of a cost-effective system.* In the next chapter, the results of this analysis are used to perform system optimizations.

The objectives of a thermoeconomic analysis are basically the following:

1. First. To understand the cost formation process and the flow costs of the system. That shows the economical increase that suffer the fuels entering the system when they are converted into products at each step of the production process until they become final products.

2. Second. To calculate the costs of each product generated by the system, that is, the cost of the sulfuric acid and the cost of the generated steam for the process considered in this thesis. It should be remarked that these costs are *real costs*, that is, the costs according to the system fuels plus operating and maintenance costs from the different processes in the production system. That means that its value has not to be equal to the price at which they should be sold in the market to obtain a desired profitability or because of the market supply and demand (see Section 5.2).

3. Third. To evaluate the costs of system inefficiencies such as the exergy destruction and exergy losses, since knowledge of these costs is very useful for improving the cost effectiveness of the system. This evaluation is more in detail explained at the end of this chapter.

During this chapter, the costs used to perform the thermoeconomic analysis are always levelized costs, although the term *levelized* is usually omitted. These costs were calculated in Chapter 4 and are convenient for such an study due to year to year cost variations.

5.1 Fundamentals of thermoeconomics

As an introduction to thermoeconomics, the following equation summarizes the methodology for evaluating a system through this type of analysis:

$$\dot{C}_{P,k} = \dot{C}_{F,k} + \dot{Z}_k^{CI} + \dot{Z}_k^{OM} \tag{5.1}$$

In this equation, the product cost rate of the kth system component at steady state, $\dot{C}_{P,k}$, is calculated as the cost rate of the fuel $\dot{C}_{F,k}$ plus the costs rates associated with capital investment and operating and maintenance costs (OAM) for the same kth component. This last sum is from now on denoted by $\dot{Z}$ [Equation (5.2)] or by *$\dot{Z}$-term*. Therefore, the product cost rates correspond always to unknowns, while fuel and $\dot{Z}$-cost rates correspond to known quantities. This type of equation, where on the left side it is found the *product term* and on the right side the *fuel term* plus the $\dot{Z}$-term is referred in this thesis as the *main cost equation*. However, when a system component presents more than one product, some auxiliary equations are needed for evaluating the product cost rates. In general terms, through this equation it can be explained that the cost rate of the *fuel*, increases its value in a value that equals the $\dot{Z}$-costs, resulting in the *product* cost rate. The cost rate units are in euros per second [euros/s] or per hour [euros/h].

$$\dot{Z} = \dot{Z}^{CI} + \dot{Z}^{OM} \tag{5.2}$$

In order to calculate the $\dot{Z}$-costs for each component, the following equations are used:

$$\dot{Z}_k^{CI} = \frac{CC_L}{\tau} \frac{PEC_k}{\sum PEC_k} \tag{5.3}$$

$$\dot{Z}_k^{OM} = \frac{OMC_L}{\tau} \frac{PEC_k}{\sum PEC_k} \tag{5.4}$$

Where CC_L and OMC_L correspond to the levelized capital recovery and levelized operating and maintenance costs, respectively, calculated in Chapter 4; τ corresponds to the number of working hours per year. In the case of the reference plant, τ equals the total hours of a whole year, that is 8,760 hours (capacity factor: 100%, Table 4.3). Table 5.1 shows the $\dot{Z}$-costs calculations.

	Purchase Cost [€]	**PEC** [%]	$\dot{Z}_k^{CI}$ [€/h]	$\dot{Z}_k^{OM}$ [€/h]	$\dot{Z}^k$ [€/h]	$\dot{Z}^k$ [€/s]
Compressor	56,100	1.9	5.19	5.06	10.2	0.00285
Sulfur Burner	248,010	8.5	22.9	22.4	45.3	0.01258
Heat Exchanger 1	614,770	21.2	56.9	55.4	112	0.03119
Heat Exchanger 2	867,440	29.9	80.2	78.2	158	0.04401
Heat Exchanger 3	57,120	2.0	5.28	5.15	10.4	0.00290
Contact Bed 1	17,450	0.6	1.61	1.57	3.19	0.00089
Contact Bed 2	436,260	15.0	40.3	39.3	79.7	0.02213
Contact Bed 3	43,630	1.5	4.03	3.93	7.97	0.00221
Absorbtion Column	561,940	19.4	52.0	50.7	103	0.02851
Total	2.902,720	100				

Table 5.1: $\dot{Z} - costs$ associated to the plant components; except to pumps, mixers, and splitters, which its purchase costs are neglected. The purchased costs are expressed in rounded mid-2008 euros.

Furthermore, a thermoeconomic evaluation for a kth system component can be also carried out using the following equation:

$$\sum_e \dot{C}_{e,k} + \dot{C}_{q,k} = \dot{C}_{w,k} + \sum_i \dot{C}_{i,k} + \dot{Z}_k \tag{5.5}$$

Here, it is taken into account more than one entering and exiting stream of matter, as well as both heat and work interactions. It should be remarked that neither all entering streams correspond to fuel streams nor all exiting streams correspond to product streams. That occurs since in some system components a fuel or a product is defined as a combination of entering and exiting streams. For that reason, it must

be defined both fuel and product for each system component (see Figures 5.2 and 5.3).

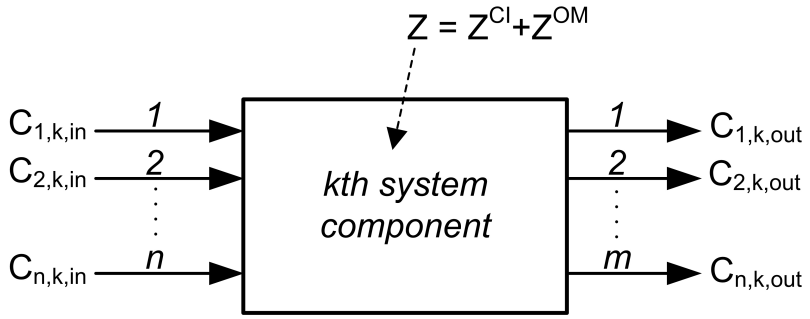


Figure 5.1: Analytic exergy costing of a system component

Equation (5.5) states that the sum of the cost rates of all exiting streams from a kth-system component, $\sum \dot{C}_{e,k}$, plus the cost rate at which heat is transferred from the system, $\dot{C}_{q,k}$, equal the sum of all entering streams into the same system component, $\sum \dot{C}_{i,k}$, plus the cost rate at which work is supplied to the system, $\dot{C}_{w,k}$, and plus the cost rate due to the capital investment and OAM costs of this component, $\dot{Z}$.

In the next section, Equation (5.5) is applied to the different system components in order to obtain firstly an analytically cost expression and later a more compact cost expression as in Equation (5.1), that is, the main cost equation. For that, it is needed to rearrange the different entering and exiting streams so as to obtain a product term on one side of the equation and a fuel term on the other side. It should be commented that in the case of a turbine for example, the work term passes to the left side of the equation with its positive sign, since now the work is an exiting stream; while In the case of a heat transfer into the system, the heat term passes to the right side of the equation also with its positive sign, since now the heat is an entering stream.

The fact of using exergy as rational basis for assigning costs to the interactions that a system experiences and to the sources of inefficiencies is known as *exergy costing*. In exergy costing a cost is associated with each exergy stream as it is showed by the following equations:

$$\dot{C}_i = c_i \dot{E}_i = c_i(\dot{m}_i e_i) \tag{5.6}$$

$$\dot{C}_e = c_e \dot{E}_e = c_e(\dot{m}_e e_e) \tag{5.7}$$

$$\dot{C}_w = c_w \dot{W} \tag{5.8}$$

$$\dot{C}_q = c_q \dot{E}_q \tag{5.9}$$

Here c_i, c_e, c_w, and c_q denote *average costs per unit of exergy* in euros per gigajoule (euros/GJ), in euros per kilowatt-hour (euros/kWh), or in cents of euro per kilowatt-hour (ct./kWh). The cost rates $\dot{C}$ and the exergy rates are expressed in euros per second (euros/s) and in kilowatts (kW), respectively.

In Equation (5.5) the unknowns are not only the exiting streams, but also the generated heat or power (e.g. turbines). For that, it is assumed that the costs per exergy unit for all entering streams are known (c_i, c_w in the case of supplying to the system with power, and c_q in the case of heat transferred into the system). After defining an exergy costing for each system component, it is obtained a system of linear equations where the number of equations (main cost equation plus auxiliary equation) must be equal to the number of unknowns. After solving this system, the cost rates of the product of each system component are obtained. Then, the average costs per unit of exergy of these streams are calculated by using Equations (5.6), (5.7), (5.8), and (5.9).

5.1.1 Costing of Exergy Loss Streams

This concept has to be introduced in a thermoeconomic analysis to take into account the monetary losses associated with the rejection of exergy from the system to its surroundings (Section 3.4). This loss costs are denoted by the term $\dot{C}_L$, so the main cost equation becomes

$$\dot{C}_{P,k} = \dot{C}_{F,k} - \dot{C}_{L,k} + \dot{Z}_k \tag{5.10}$$

As Equations (5.6), (5.7), (5.8), and (5.9) present the relation between the cost rate and the exergy associated to different type of streams, now for the case of exergy losses it is usually needed also a relation. However, not all exery losses in a system have to imply additional relations. For example, it could happen that an exiting stream from a system component is costed as a part of the fuel component, but even so, this stream represents an exergy loss for the whole process. In this case, no addition relations are needed for costing the exergy loss, since it is already costed as part of this fuel. That happens in the third heat exchanger of this thesis, where

stream 33 forms part of the fuel and at the same time, represents an exergy loss for the sulfuric acid plant.

Two type of exergy loss approaches are reviewed:

1. This first approach states that the exergy losses associated with a kth component present cost zero [Equation (5.11)]. With this simple relation, the product bears all expenses associated with this component. This approach is used when the purpose of the thermoeconomic analysis is to calculate the final products or to optimize the overall system. In this thesis, this relation is used in the absorbtion column, where the stack gases represent exergy losses.

$$\dot{C}_{L,k} = 0 \tag{5.11}$$

2. This second approach states that the exergy losses of the kth component are costed as if they were fuel [Equation (5.12)], so it represents the additional fuel costs that have to be supplied to the component to cover this loss. This approach is used when the purpose is to understand the cost formation of the process and the cost flow in the system, as well as to study the performance of a component or its own optimization, for example by reducing the exergy losses. In the calculations, it is assumed that the average costs per unit of fuel exergy of a component remain constant with varying exergy loss.

$$\dot{C}_{L,k} = c_{F,k}\dot{E}_{L,k} \tag{5.12}$$

At the end of the thermoeconomic analysis, once all streams are costed, the expenses due to exergy losses have to be carried by the final products of the plant. However, in this thesis, it is only carried by the sulfuric acid, since from a point of view of the plant main purpose, it is assumed that this product is more outstanding than the generated vapor steam.

5.1.2 Exergy Costing for the Considered Process Components

In this section, it is explained how the thermodynamic analysis for each type of component in the sulfuric acid plant is carried out. The components reviewed in this section are: *compressors and pumps, sulfur burners, heat exchangers, contact beds,*

absorbtion columns, mixers, and splitters. First, for each component, an exergy costing equation is defined using Equation (5.5), and later, after rearranging the terms and using the fuel and product definitions from Figures 5.2 and 5.3, the main cost equation for that component is defined.

Compressors and Pumps

Adiabatic compressors and pumps are considered, with the following analytical equation:

$$\dot{C}_2 = \dot{C}_{w,comp} + \dot{C}_1 + \dot{Z}_{comp} \tag{5.13}$$

So rearranging the terms according to the definition of fuel and product in compressors (Figure 5.2) it yields the following main cost equation:

$$(\dot{C}_2 - \dot{C}_1) = \dot{C}_{w,comp} + \dot{Z}_{comp} \tag{5.14}$$

In this second equation, the term *product* is identified on the left side as the difference between the cost rate of the exiting stream minus the cost rate of the entering stream. The term *fuel* is the cost rate due to required work, $\dot{C}_{w,comp}$. In this case, the only unknown is $\dot{C}_2$, so no auxiliary equations are required. It is supposed that the cost rate of the entering stream, $\dot{C}_1$, the price at which the electricity supply is payed, c_w, and the $\dot{Z}$-term of the compressor are known. This value was calculated in the last section [Equation (4.37)].

Sulfur Burners

In this work, sulfur burners are considered adiabatic with the following analytical equation:

$$\dot{C}_3 = \dot{C}_1 + \dot{C}_2 + \dot{Z}_{sburn} \tag{5.15}$$

Rearranging the terms according to the definition of fuel and product in sulfur burners (Figure 5.2) it yields the following main cost equation:

$$\dot{C}_3 = (\dot{C}_1 + \dot{C}_2) + \dot{Z}_{sburn} \tag{5.16}$$

In this case, for the cost main equation, it is not needed to rearrange the terms, but to put in brackets the two entering streams just in order to emphasize that its sum corresponds to the fuel term of the sulfur burner. Sulfur burners present only one

unknown, $\dot{C}_3$, so no auxiliary equations are needed. The cost rates of both entering sulfurous, $\dot{C}_1$, and air streams, $\dot{C}_2$, have to be previously known before calculating the product cost rate.

Heat Exchangers

As shown in Figure 5.2, two type of heat exchangers according to its thermal objective can be considered: Heat exchangers which heat an entering stream, type *a*, or heat exchangers which cool an entering stream, type *b*. Equation (5.17) shows the analytical expression for both type of heat exchangers, since the difference between them lies only in its main cost equation. The cold stream is indicated with the subindexes 1 and 2, while the hot stream with the subindexes 3 and 4.

$$\dot{C}_2 + \dot{C}_4 = \dot{C}_1 + \dot{C}_3 + \dot{Z}_{hx} \tag{5.17}$$

Rearranging the terms for the type *a* and for the type *b*, Equations (5.18) and (5.19) are obtained, respectively.

$$(\dot{C}_2 - \dot{C}_1) = (\dot{C}_3 - \dot{C}_4) + \dot{Z}_{hxa} \tag{5.18}$$

$$(\dot{C}_4 - \dot{C}_3) = (\dot{C}_1 - \dot{C}_2) + \dot{Z}_{hxb} \tag{5.19}$$

In the first case, heat exchanger of the type *a*, the product consists of the exergy increase in the entering cold stream, $\dot{C}_2 - \dot{C}_1$, while the fuel consists of the exergy decrease in the entering hot stream, $\dot{C}_3 - \dot{C}_4$. Both increase and decrease have positive sign. In the second case, heat exchanger of the type *b*, the product consists of the exergy decrease in the entering hot stream, $\dot{C}_4 - \dot{C}_3$, while the fuel consists of the exergy increase in the entering cold stream, $\dot{C}_1 - \dot{C}_2$. Both decrease and increase have negative sign.

Heat exchangers always need one auxiliary equation, since they present two unknowns, both exiting cold and hot stream. Usually, this auxiliary equation is presented by an equality which says that the average cost per unit of both fuel's entering and exiting exergy streams remains constant [Equation (5.20) for type *a*, Equation (5.21) for type *b*]. This expression reflects that in both heat exchangers the fuel does not gain in average cost per exergy, but the product.

$$c_4 = c_3 \quad (type\ a) \tag{5.20}$$

$$c_2 = c_1 \quad (type\ b) \tag{5.21}$$

In the case of producing steam at the same time that the product stream is being heated or cooled, conceptually, it is not right to use Equations (5.20) and (5.20), since now there is more than one product. For this case, in this thesis, the following approaches are used:

$$\frac{\dot{C}_3 - \dot{C}_4}{\dot{E}_4 - \dot{E}_3} = \alpha \frac{\dot{C}_2 - \dot{C}_1}{\dot{E}_2 - \dot{E}_1} \quad (type\ a) \tag{5.22}$$

$$\frac{\dot{C}_1 - \dot{C}_2}{\dot{E}_1 - \dot{E}_2} = \alpha \frac{\dot{C}_4 - \dot{C}_3}{\dot{E}_3 - \dot{E}_4} \quad (type\ b) \tag{5.23}$$

These expressions state that the average cost per unit of exergy of the steam generated, on the left side of the equations, equals the average cost per unit of exergy of the heat exchanger main product, on the right side of the equations, weighted by a factor, α. This factor approaches how important is considered the steam in the heat exchanger where it is generated; that is, the more important is the steam, the more the $\dot{Z}$-expenses are distributed between both products. In this work, an α-factor of 0.6 is chosen.

The cost rates of both entering cold and hot streams, $\dot{C}_1$ and $\dot{C}_3$ respectively, have to be previously known before calculating the product cost rates.

Contact Beds

Contact beds present a simple exergy costing equation, since there is only one entering and exiting stream. Therefore, the main exergy costing equation is equal to its analytical version [Equation (5.24)].

$$\dot{C}_2 = \dot{C}_1 + \dot{Z} \tag{5.24}$$

There is only one unknown, the product cost rate $\dot{C}_2$, so no auxiliary equations are needed.

Absorbtion Column

In the absorbtion column there are two entering streams: the SO_3 stream (stream *1*) and the recirculating sulfuric acid stream (stream *2*); and two exiting streams: the 78 wt% sulfuric acid (stream *3*) and the stack gases (stream *4*), which are considered an exergy loss. One auxiliary equation is needed due to this last stream [Equation

(5.27)]. The analytical exergy costing equation is the following:

$$\dot{C}_3 + \dot{C}_4 = \dot{C}_1 + \dot{C}_2 + \dot{Z}_{abs} \tag{5.25}$$

That yields the following main cost equation (see Table 5.3):

$$\dot{C}_3 - \dot{C}_2 = \dot{C}_1 - \dot{C}_4 + \dot{Z}_{abs} \tag{5.26}$$

The term $\dot{C}_4$ corresponds to the expenses due to the waste of exergy, that is, exergy losses, since this stream is not used by any other component of the plant and then, it is wasted to the environment. As explained in Section 5.1.1, the exergy losses due to the stack gasses are costed with Equation (5.11), so both cost rate and average cost per unit of loss of exergy present zero value. Consequently, the whole component expenses are carried by the product ($\dot{C}_3$-$\dot{C}_2$). The reason of using the first exergy loss approach lies in that the costing for this component is focused on its product, which is directly related with the main plant final product (Stream *12*). In further studies, it could be interesting to cost the losses by using the second approach. In that hypothetical case, it should be remarked that the average cost per unit of exergy loss would present a high value, since the absorber is located at the end of the plant process and fuel costs tend to be higher in upstream processes (Section 5.2).

$$\dot{C}_4 = \dot{C}_{L,abs} = 0 \tag{5.27}$$

It should be remarked that the product in the absorber is not taken as only the 78 wt% sulfuric acid stream, but the difference between this last stream and the recycling acid stream. The reason is that when a stream crosses the boundary of a system twice with no change in chemical composition -at steady state, the molar composition of the 78 wt% sulfuric acid is quite close to the molar composition of the recycling acid- only the difference in the exergy values of the stream should be considered in the calculation of the fuel or product. In this case, where the stream difference refers to the product, it is said that this difference is known as the *net* exergy supplied *to* the product [5].

The absorbtion column presents only one unknown, $\dot{C}_3$, so no auxiliary equations are needed, apart of approaching the exergy loss cost rates by Equation (5.27). The cost rates of entering streams, $\dot{C}_1$ and $\dot{C}_2$, have to be known from previous calculations in upstream components.

Mixers

The mixers are simple components with only one product, which consists of the mixture of two streams, and null $\dot{Z}$-costs, since the capital investment and the expenses due to operation and maintenance are neglected. The analytical exergy costing equation corresponds to its main product equation:

$$\dot{C}_3 = \dot{C}_1 + \dot{C}_2 \tag{5.28}$$

The cost rates of the two entering streams have to be previously known and no auxiliary equations are needed.

Splitters

This type of component splits an entering stream, the fuel, into two exiting streams, two products [Equation (5.29)]. As in the mixer, the $\dot{Z}$-costs are also neglected, with the difference that now one auxiliary equation is needed [Equation (5.30)]. This auxiliary equation states that the average cost per unit of the entering exergy equals the average costs of both exiting streams.

$$\dot{C}_2 + \dot{C}_3 = \dot{C}_1 \tag{5.29}$$

$$c_2 = c_1 \tag{5.30}$$

5.2 Thermoeconomic analysis of the Considered Process

Once the cost formation process for each system component is understood through the exergy costing theory, it can be written a linear equation system with all component main cost equations and its respective auxiliary equations. In order to verify if this equation system can be solved, the total number of equations must be equal to the number of streams. By replacing the cost stream numbers of the equations from last section with its corresponding flow numbers in the considered process -Compressor, pump 1, and pump 2 power streams are numbered as streams *34*, *35*, and *36*, respectively-, the following equation system is obtained:

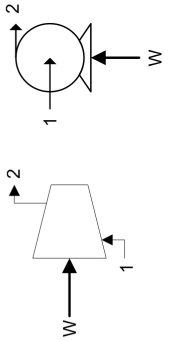
Component	Compressor, or Fan	Sulfur Burner	Heat Exchanger Type a	Heat Exchanger Type b
Schematic				
Cost rate of product (C_P)	$C_2 - C_1$	C_3	$C_2 - C_1$	$C_4 - C_3$
Cost rate of fuel (C_F)	C_W	$C_1 + C_2$	$C_3 - C_4$	$C_1 - C_2$
Auxiliary equations	None	None	$\frac{C_3 - C_4}{E_4 - E_3} = \alpha \frac{C_2 - C_1}{E_2 - E_1}$	$\frac{C_1 - C_2}{E_1 - E_2} = \alpha \frac{C_4 - C_3}{E_3 - E_4}$ or $c_3 = c_4$	or $c_1 = c_2$
Variables calculated from Exergy costing	C_2, c_2	C_3, c_3	C_2, c_2	C_4, c_4

Figure 5.2: Cost rates associated with fuel and product, and auxiliary exergy costing relations

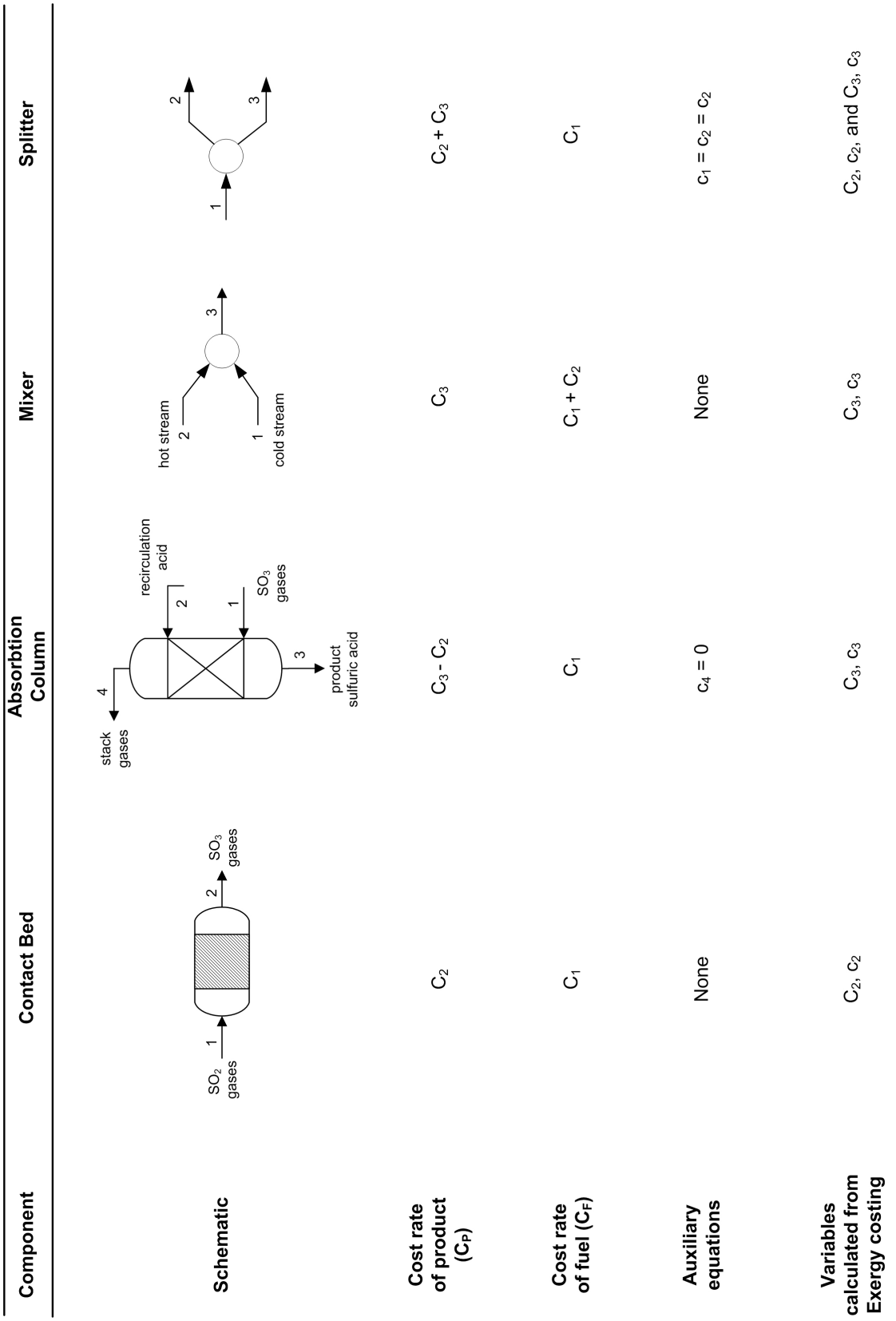


Figure 5.3: Cost rates associated with fuel and product, and auxiliary exergy costing relations

Compressors and Pumps

$$Compressor \qquad \dot{C}_{18} = \dot{C}_{w,comp} + \dot{C}_{17} + \dot{Z}_{comp} \tag{5.31}$$

$$Pump1 \qquad \dot{C}_{11} = \dot{C}_{w,pump1} + \dot{C}_{10} \tag{5.32}$$

$$Pump2 \qquad \dot{C}_{30} = \dot{C}_{w,pump2} + \dot{C}_{29} \tag{5.33}$$

$$\frac{\dot{C}_{w,comp}}{\dot{W}_{comp}} = \frac{\dot{C}_{w,pump1}}{\dot{W}_{pump1}} = \frac{\dot{C}_{w,pump2}}{\dot{W}_{pump2}} = c_w \tag{5.34}$$

$$c_w = 0.1609 \text{ euros/kWh}^1 \tag{5.35}$$

Sulfur Burners

$$\dot{C}_2 = \dot{C}_1 + \dot{C}_{19} + \dot{Z}_{sburn} \tag{5.36}$$

Heat Exchangers

$$Heat\ Exchanger\ 1 \qquad (\dot{C}_3 - \dot{C}_2) = (\dot{C}_{25} - \dot{C}_{26}) + \dot{Z}_{hx1} \tag{5.37}$$

$$\frac{\dot{C}_{26} - \dot{C}_{25}}{\dot{E}_{26} - \dot{E}_{25}} = 0.6\frac{\dot{C}_3 - \dot{C}_2}{\dot{E}_2 - \dot{E}_3} \tag{5.38}$$

$$Heat\ Exchanger\ 2 \qquad (\dot{C}_9 - \dot{C}_8) = (\dot{C}_{27} - \dot{C}_{28}) + \dot{Z}_{hx2} \tag{5.39}$$

$$\frac{\dot{C}_{28} - \dot{C}_{27}}{\dot{E}_{28} - \dot{E}_{27}} = 0.6\frac{\dot{C}_9 - \dot{C}_8}{\dot{E}_8 - \dot{E}_9} \tag{5.40}$$

$$Heat\ Exchanger\ 3 \qquad (\dot{C}_{15} - \dot{C}_{14}) = (\dot{C}_{31} - \dot{C}_{33}) + \dot{Z}_{hx3} \tag{5.41}$$

$$\frac{\dot{C}_{33}}{\dot{E}_{33}} = \frac{\dot{C}_{31}}{\dot{E}_{31}} \tag{5.42}$$

[1] Equation (4.37)

Contact Beds

$$Contact\ Bed\ 1 \qquad \dot{C}_4 = \dot{C}_3 + \dot{Z}_{bed1} \tag{5.43}$$

$$Contact\ Bed\ 2 \qquad \dot{C}_6 = \dot{C}_5 + \dot{Z}_{bed2} \tag{5.44}$$

$$Contact\ Bed\ 3 \qquad \dot{C}_8 = \dot{C}_7 + \dot{Z}_{bed3} \tag{5.45}$$

Absorbtion Columns

$$\dot{C}_{10} = \dot{C}_9 + \dot{C}_{15} - \dot{C}_{16} + \dot{Z_a bs} \tag{5.46}$$

$$\frac{\dot{C}_{16}}{\dot{E}_{16}} = 0 \tag{5.47}$$

Mixers

$$Mixer\ 1 \qquad \dot{C}_5 = \dot{C}_4 + \dot{C}_{21} \tag{5.48}$$

$$Mixer\ 2 \qquad \dot{C}_7 = \dot{C}_6 + \dot{C}_{23} \tag{5.49}$$

$$Mixer\ 3 \qquad \dot{C}_{14} = \dot{C}_{13} + \dot{C}_{32} \tag{5.50}$$

Splitters

$$Splitter\ 1 \qquad \dot{C}_2 + \dot{C}_3 = \dot{C}_1 \tag{5.51}$$

$$\frac{\dot{C}_2}{\dot{E}_2} = \frac{\dot{C}_1}{\dot{E}_1} \tag{5.52}$$

$$Splitter\ 2 \qquad \dot{C}_{21} + \dot{C}_{22} = \dot{C}_{20} \tag{5.53}$$

$$\frac{\dot{C}_{21}}{\dot{E}_{21}} = \frac{\dot{C}_{20}}{\dot{E}_{20}} \tag{5.54}$$

$$Splitter\ 3 \qquad \dot{C}_{23} + \dot{C}_{24} = \dot{C}_{22} \tag{5.55}$$

$$\frac{\dot{C}_{23}}{\dot{E}_{23}} = \frac{\dot{C}_{22}}{\dot{E}_{22}} \tag{5.56}$$

$$\textit{Splitter } 4 \qquad \dot{C}_{12} + \dot{C}_{13} = \dot{C}_{11} \tag{5.57}$$

$$\frac{\dot{C}_{12}}{\dot{E}_{12}} = \frac{\dot{C}_{11}}{\dot{E}_{11}} \tag{5.58}$$

$$\textit{Splitter } 5 \qquad \dot{C}_{31} + \dot{C}_{32} = \dot{C}_{30} \tag{5.59}$$

$$\frac{\dot{C}_{31}}{\dot{E}_{31}} = \frac{\dot{C}_{30}}{\dot{E}_{30}} \tag{5.60}$$

Other Auxiliary Relations

$$\frac{\dot{C}_{1}}{\dot{E}_{1}} = 0 \tag{5.61}$$

$$\frac{\dot{C}_{17}}{\dot{E}_{17}} = 0 \tag{5.62}$$

$$\frac{\dot{C}_{25}}{\dot{E}_{25}} = \frac{\dot{C}_{27}}{\dot{E}_{27}} = \frac{\dot{C}_{29}}{\dot{E}_{29}} = 0 \tag{5.63}$$

The system has 36 equations and 36 unknowns, so it has a unique solution. The group of equations called *Other Auxiliary Relations* set the values of the entering streams into the plant, which in fact are parameters. This relations state that the average cost per unit of exergy of the entering sour gas, process water, and atmospheric air are taken null, since they are considered as free of charges. In further studies, the costs related to the entering process streams could be approached by values different to zero in order to obtain a more realistic thermoeconomic analysis. That would take into account, for example, the fact that the entering sour gas could carry expenses from upstream processes; as well as the possibility of setting non-zero values in the cost rates of entering atmospheric air and process water due to previous cleaning and drying treatments.

The linear equation system is solved with MATLAB, yielding the results (intermediate case) shown in the following tables:

Tables 5.2, 5.3, and 5.4 present the solution of the equation system, which consist of the cost rate values in euros per second from all system streams, as well as its

	Stream nº	$\dot{E}_{tot}$ **[MW]**	**c [euro/GJ]**	**c [ct./kWh]**	$\dot{C}$ **[euro/h]**
Sour gas	1	5.94	0.000	0.000	0.00
SO_2 from c. chamber	2	4.43	3.851	1.386	61.4
SO_2 from boiler	3	2.22	18.14	6.532	145
SO_3 from horde 1	4	2.18	18.89	6.802	148
SO_3 from quench 1	5	2.07	20.88	7.518	156
SO_3 from horde 2	6	2.03	32.24	11.61	235
SO_3 from quench 2	7	1.99	33.13	11.93	238
SO_3 from horde 3	8	1.99	34.34	12.36	246
SO_3 from boiler	9	1.40	70.58	25.41	356
H_2SO_4 from absorbtion	10	39.0	197.8	71.22	27,768
H_2SO_4 from pump	11	39.0	197.8	71.22	27,768
H_2SO_4 to sell	12	0.66	197.8	71.22	470
H_2SO_4 to recirculate	13	38.3	197.8	71.22	27,298
H_2SO_4 mixed with water	14	38.3	198.0	71.28	27.298
H_2SO_4 from heat-exchanger	15	38.1	199.3	71.74	27,309
Stack gas	16	0.04	0.000	0.000	0.00

Table 5.2: Thermoeconomic results for the reference plant: main stream (Intermediate case)

	Stream n°	$\dot{E}_{tot}$ **[MW]**	**c [euro/GJ]**	**c [ct./kWh]**	$\dot{C}$ **[euro/h]**
Atmospheric air	17	0.00	0.000	0.000	0.00
Air from compressor	18	0.07	105.4	37.94	26.1
Air to combustion	19	0.04	105.4	37.94	16.1
Air	20	0.03	105.4	37.94	10.0
Air to quench 1	21	0.02	105.4	37.94	7.42
Air	22	0.01	105.4	37.94	2.54
Air to quench 2	23	0.01	105.4	37.94	2.54
Air released	24	0.00	0.000	0.000	0.00
Water to boiler 1	25	0.05	0.000	0.000	0.00
Vapor from boiler 1	26	1.31	6.067	2.184	28.7
Water to boiler 2	27	0.02	0.000	0.000	0.00
Vapor from boiler 2	28	0.44	29.96	10.79	47.7
Water to pump	29	0.36	0.000	0.000	0.00
Water from pump	30	0.36	0.184	0.066	0.24
Water to heat exchanger	31	0.36	0.184	0.066	0.24
Water to mixer	32	0.00	0.184	0.066	0.00
Water from heat exchanger	33	0.36	0.184	0.066	0.24

Table 5.3: Thermoeconomic results for the reference plant: atmospheric air and water (Intermediate case)

	Stream nº	$\dot{E}_{tot}$ **[MW]**	**c [euro/GJ]**	**c [ct./kWh]**	$\dot{C}$ **[euro/h]**
Compressor	34	0.099	44.69	16.09	15.9
Pump 1	35	0.000	44.69	16.09	0.04
Pump 2	36	0.001	44.69	16.09	0.24

Table 5.4: Costs associated with compressor and pumps power for the reference plant (Intermediate case)

corresponding average cost rates. These last costs are obtained by using Equations (5.6), (5.7), and (5.8).

It is a fact that the costs increase in upper streams. The reason is that when a same stream enters and exists several components, the expenses of each component ($\dot{Z}$-costs) are carried by the exiting streams, so at the end, the more one stream through different components flows, the more expensive the costs associated to this stream are. That is also related with the fact, that if all calculations are correctly done, the exiting streams from the system should burden the whole charges associated with the production process of sulfuric acid. In that case, this charges equal the levelized total required revenue, TRR_L, calculated in Section 4.4, and which is distributed into system components through a CC_L and OMC_L-terms [see Equations (5.3) and (5.4)].

Furthermore, it is interesting to remark that, on one hand, by means of an economic analysis (Chapter 4), the TRR_L is afforded by the revenue obtained through the sale of both sulfuric acid and generated steam plant products, according to an established market price in relation with steam prices. Since the selling price of the vapor steam at 40 bar and 5 bar is considered having respectively a value of 4.6 euros/kg and 3.4 euros/kg (Table 5.6), the selling price of the sulfuric acid produced in the plant can be calculated (Section 4.4). On the other hand, through the thermoeconomic analysis, the *real* cost of these products can be known, which in simpler words means how much money implies to manufacture a desired product without any market regulation. This concept is useful in order to study the economic profitability of the plant.

Thermoeconomic	**Favorable**	**Intermediate**	**Unfavorable**
H_2SO_4	15.5	18.2	22.2
Steam (40 bar)	0.52	0.61	0.75
Steam (5 bar)	1.90	2.24	2.75
Economic	**Favorable**	**Intermediate**	**Unfavorable**
H_2SO_4	6.90	10.0	14.7
Steam (40 bar)	4.60	4.60	4.60
Steam (5 bar)	3.40	3.40	3.40

Table 5.5: Product prices in cents of euro per kilogram of both thermoeconomic and economic analysis for the reference plant. The differences in H_2SO_4 prices are due to fact that the steam prices are different in both analyses

From Table 5.5, it is observed that the cost of the sulfuric acid obtained by the thermoeconomic analysis is higher than the cost obtained by the economic analysis. That means that the production of sulfuric acid in the plant is more expensive than the price at which it should be sold in the market. On the other hand, the cost of the steam at 40 and 5 bar in both cases is lower than its corresponding market price, so the loss of money from selling the sulfuric acid is balanced by the sales of steam. The price difference between both studies is explained by the fact that the costs given to the process steam in the thermoeconomic analysis are only an approach: the vapor steam exiting the heat exchangers carries symbolically operating and maintenance costs [Equation (5.38) and (5.40)] by means of the α-factor. At this point, it should be remarked that the α-factor could be set for both first and second heat exchangers to that values that would yield the same plant product prices for both thermoeconomic and economic analyses. Nevertheless, in this thesis, these factors are set in a way (α=0.6) that the sulfurous streams, which at the end of the process become the product sulfuric acid, carry the most of the plant costs.

Table 5.6 compares the annual revenues by the sale of the plant products between an economic and a thermoeconomic analysis, so the total revenue obtained from both analysis should equal the TRR_L. The total revenue of the thermoeconomic analysis yields an error of 0.001% [Equation (5.64)], so it is stated that there is no error in the thermoeconomic calculations.

$$\frac{4.785,150 - 4.785,120}{4.785,150} \cdot 100 = 0.001\ \% \tag{5.64}$$

Additionally, it should be remarked that the value corresponding to the final sulfuric acid (stream *12*) in Table 5.2 differs slightly from the value in Table 5.6, since this last value, $\dot{C}^*_{H_2SO_4}$, includes the expenses due to exergy losses [Equation (5.65)].

$$\begin{gathered}
\dot{C}^*_{H_2SO_4} = \dot{C}_{H_2SO_4} + \dot{C}_{L,hx3} \\
\dot{C}_{L,hx3} = \dot{C}_{33} \\
\dot{C}^*_{H_2SO_4} = 470 + 0.24 = 470.24 \text{ euros/h} \\
c^*_{H_2SO_4} = (\dot{C}_{H_2SO_4} + \dot{C}_{33})/E_{H_2SO_4} \\
c^*_{H_2SO_4} = 470.24/0.66 \cdot 0.1 = 71.26 \text{ ct./kWh}
\end{gathered} \tag{5.65}$$

5.3 Thermoeconomic Variables

After solving the linear equation system comprised from Equation (5.31) to Equation (5.63), there is a group of variables that have to be taken into account in order to understand more properly the thermoeconomic evaluation and furthermore, optimize the system. This variables are known as *thermoeconomic variables* and are summarized in Table 5.8 [5]:

- (a) The average unit cost of fuel, $c_{F,k}$.
- (b) The average unit cost of product, $c_{P,k}$.
- (c) The cost rate of exergy destruction, $\dot{C}_{D,k}$.
- (d) The exergoeconomic factor, f_k.

5.3.1 Average Unit Cost of Fuel and Product

The average unit cost of fuel and product from the kth system component are calculated by using the definitions shown in Figures 5.2 and 5.3 with Equations (5.66) and (5.67), respectively. The results are presented in Table 5.7.

$$c_{F,k} = \frac{\dot{C}_{F,k}}{E_{F,k}} \tag{5.66}$$

$$c_{P,k} = \frac{\dot{C}_{P,k}}{E_{P,k}} \tag{5.67}$$

5.3.2 Cost Rate of Exergy Destruction

Since now, the exergy destruction cost rate has not appeared in exergy costing equations. The reason is that the cost associated to the exergy destruction in a component is a *hidden cost*, which can only be revealed combining equations from both thermoeconomic and exergetic analysis. This variable can be considered the most important in a thermoeconomic analysis. Table 5.8 shows the exergy destruction rates from all system components.

In chapter 3, the exergy destruction rate is calculated for each plant component using Equation (5.68); here, exergy losses are also taken into account. Therefore, if this equation is combined with the main cost equation of the kth component of the

Economic analysis	$\dot{E}$ **[MWh/year]**	$\mathbf{c}_E$ **[ct./kWh]**	$\dot{C}$ **[euros/year]**	$\dot{m}$ **[kg/h]**	$\mathbf{c}_E$ **[ct./kg]**	$\dot{C}$ **[euros/year]**
Sulfuric acid	5,780	39.21	2.264,580	2,580	10.02	2.264,580
Steam (40 bar)	11,520	16.37	1.885,750	4,680	4.60	1.885,750
Steam (5 bar)	3,880	16.37	634,820	2,130	3.40	634,820
Total			4.785,150			4.785,150
Thermoeconomic analysis	**[MWh/year]**	**[ct./kWh]**	**[euros/year]**	**[kg/h]**	**[ct./kg]**	**[euros/year]**
Sulfuric acid	5,780	71.26	4.115,670	2,580	18.21	4.115,670
Steam (40 bar)	11,520	2.18	251,090	4,680	0.61	251,090
Steam (5 bar)	3,880	10.79	418,360	2,130	2.24	418,360
Total			4.785,120			4.785,120

Table 5.6: Rounded average costs per unit of exergy of the plant products calculated through an economic and a thermoeconomic analysis for the reference plant (Intermediate case). The terms c_E and c_m correspond to the specific costs per exergy and mass, respectively.

	Fuel	c_F [€/GJ]	c_F [ct./kWh]	Product	c_P [€/GJ]	c_P [ct./kWh]
Compressor	C_{34}/W_{comp}	44.7	16.1	$(C_{18}\text{-}C_{17})/(E_{18}\text{-}E_{17})$	102	36.6
Sulfur burner	$(C_1+C_{19})/(E_1+E_{19})$	0.75	0.27	C_2/E_2	3.85	1.39
Heat exchanger 1	$(C_{26}\text{-}C_{25})/(E_{26}\text{-}E_{25})$	6.29	2.27	$(C_3\text{-}C_2)/(E_2\text{-}E_3)$	10.5	3.78
Contact bed 1	C_3/E_3	18.1	6.53	C_4/E_4	18.9	6.80
Mixer 1	$(C_4+C_{21})/(E_4+E_{21})$	19.7	7.08	C_5/E_5	20.9	7.52
Contact bed 2	C_5/E_5	20.9	7.52	C_6/E_6	32.2	11.6
Mixer 2	$(C_6+C_{23})/(E_6+E_{23})$	32.5	11.7	C_7/E_7	33.1	11.9
Contact bed 3	C_7/E_7	33.1	11.9	C_8/E_8	34.3	12.4
Heat exchanger 2	$(C_{28}\text{-}C_{27})/(E_{28}\text{-}E_{27})$	31.5	11.3	$(C_9\text{-}C_8)/(E_8\text{-}E_9)$	52.5	18.9
Absorbtion column	C_9/E_9	70.6	25.4	$(C_{10}\text{-}C_{15})/(E_{10}\text{-}E_{15})$	138	49.7
Pump 1	C_{35}/W_{pump1}	44.7	16.1	$(C_{11}\text{-}C_{10})/(E_{11}\text{-}E_{10})$	0.00	0.00
Pump 2	C_{36}/W_{pump2}	44.7	16.1	$(C_{30}\text{-}C_{29})/(E_{30}\text{-}E_{29})$	0.00	0.00
Mixer 3	$(C_{13}+C_{32})/(E_{13}+E_{32})$	198	71.2	C_{14}/E_{14}	198	71.3
Heat exchanger 3	$(C_{33}\text{-}C_{31})/(E_{33}\text{-}E_{31})$	0.2	0.1	$(C_{15}\text{-}C_{14})/(E_{14}\text{-}E_{15})$	12.5	4.49

Table 5.7: Definition and average costs of the fuel and product from all system components for the reference plant (Intermediate case)

plant [Equation (5.69)], by eliminating the term $\dot{E}_{F,k}$, that yields a new equation where now the exergy destruction rate is costed at the average fuel cost [Equations (5.70) and (5.72)]. It should be remarked, that it is also possible to eliminate the term $\dot{E}_{P,k}$ from Equation (5.69) in order to obtain an alternative equation where the exergy destruction rate is costed at the average product cost [Equations (5.71) and (5.73)]. In this thesis, to understand the influence of exergy destruction in the cost formation of the plant, the first approach is taken.

$$\dot{E}_{F,k} = \dot{E}_{P,k} + \dot{E}_{L,k} + \dot{E}_{D,k} \tag{5.68}$$

$$c_{P,k}\dot{E}_{P,k} = c_{F,k}\dot{E}_{F,k} - \dot{C}_{L,k} + \dot{Z}_k \tag{5.69}$$

$$c_{P,k}\dot{E}_{P,k} = c_{F,k}\dot{E}_{P,k} + \dot{Z}_k + (c_{F,k}\dot{E}_{L,k} - \dot{C}_{L,k}) + c_{F,k}\dot{E}_{D,k} \tag{5.70}$$

$$c_{P,k}\dot{E}_{P,k} = c_{F,k}\dot{E}_{F,k} + \dot{Z}_k + (c_{P,k}\dot{E}_{L,k} - \dot{C}_{L,k}) + c_{P,k}\dot{E}_{D,k} \tag{5.71}$$

$$\dot{C}_{D,k} = c_{F,k}\dot{E}_{D,k}, \qquad \dot{E}_{P,k} \;\; fixed \tag{5.72}$$

$$\dot{C}_{D,k} = c_{P,k}\dot{E}_{D,k}, \qquad \dot{E}_{F,k} \;\; fixed \tag{5.73}$$

Furthermore, it is interesting to observe that in the case of a system component that does not present neither exergy destruction nor exergy losses, the average product rate equals the fuel average rate plus the $\dot{Z}$-costs of that component per unit of product exergy. This fact is clearly appreciated in Equation (5.75), which states that if it is considered a constant value $c_{F,k}$, the average cost per unit of product exergy depends only on the operating and maintenance expenses corresponding to the component. Nevertheless, in the general case of not agreeing with this statement [Equation (5.74)], it is observed that the average product cost is also related with exergy losses and exergy destruction according to the following implications:

1. *Exergy loss.* The exergy losses are carried by the average cost of the product associated to the same component in a way which depends on the difference between the exergy losses costed as fuel and its real value (term $c_{F,k}\dot{E}_{L,k} - \dot{C}_{L,k}$); that is, the value obtained from the thermoeconomic analysis (see Section 5.1.1). So, on one hand, if in such an analysis the exergy losses in a component are considered having cost zero, consequently the whole exergy loss expenses are added to the average product cost. On the other hand, if they are costed at the average fuel cost, they are not included in the product cost.

2. *Exergy destruction.* For a fixed $c_{F,k}$ and component exergetic efficiency values (Section 3.5), it can be understood as the additional fuel that has to be supplied to a component in order to obtain an specific product, $\dot{E}_{P,k}$. This definition is the same as the definition given to the cost rates due to exergy losses in Section 5.1.1 (second approach), but now it is just due to component inefficiencies.

   This term is very important for the analysis because it helps to understand how a component might be improved. As Equation (5.76) shows, it happens that in most of the components there are not exergy losses, so the average product cost depends only on $\dot{Z}$- and exergy destruction costs. That states the following phenomenon: For most system components, the higher the exergetic efficiency is, the lower the exergy destruction, which implies an increase in the $\dot{Z}$-costs and a reduction due to exergy destruction expenses [5]. This fact is more in detail reviewed in the next section and it establishes the basis of the optimization methodology carried out in the next chapter, which tries to find the appropriate trade-offs between $C_{D,k}$ and $\dot{Z}_k$ in order to improve the cost effectiveness of the system. The costs contributions from investment and exergy destruction to the average product cost are referred in this thesis as the specific expenses $c^Z_{P,k}$ and $c^{ED}_{P,k}$, respectively [Equations (5.77) and (5.78)].

$$c_{P,k} = c_{F,k} + \frac{\dot{Z}_k + (c_{F,k}\dot{E}_{L,k} - \dot{C}_{L,k}) + c_{F,k}\dot{E}_{D,k}}{\dot{E}_{P,k}} \tag{5.74}$$

$$\dot{E}_{D,k} = \dot{E}_{L,k} = 0, \qquad c_{P,k} = c_{F,k} + \underbrace{\frac{\dot{Z}_k}{\dot{E}_{P,k}}}_{c^Z_{P,k}} \tag{5.75}$$

$$c_{P,k} = c_{F,k} + \underbrace{\frac{\dot{Z}_k + c_{F,k}\dot{E}_{D,k}}{\dot{E}_{P,k}}}_{c^Z_{P,k}+c^{ED}_{P,k}} \tag{5.76}$$

$$c^Z_{P,k} = \frac{\dot{Z}_k}{\dot{E}_{P,k}} \tag{5.77}$$

$$c^{ED}_{P,k} = \frac{c_{F,k}\dot{E}_{D,k}}{\dot{E}_{P,k}} \tag{5.78}$$

Additionally, it is also of interest to notice the fact that in a thermoeconomic analysis the specific product cost increases with increasing exergy destruction and exergy loss. In other circumstances, product costs might be sunk only by decreasing the

$\dot{Z}$-costs, even if the exergy destruction and exergy losses rates had unusual values. Accordingly, it might be said that a thermoeconomic analysis is an ethical method which suggests to avoid both vast amounts of fuel, in the case of not having limits on exergy destruction, and waste streams to the environment, which possibly might be used in further processes or otherwise might be polluting.

5.3.3 Exergoeconomic Factor

As explained in the previous section, the cost sources from a system component are due to investment costs and both exergetic destruction and loss. Thus, the exergoeconomic factor [Equation (5.79)] expresses the contribution of the capital cost to the sum of capital cost and cost of exergy destruction in a system component [9]. The f-factor values for all system components are shown in Table 5.8.

$$f_k = \frac{\dot{Z}_k}{\dot{Z}_k + c_{F,k}\dot{E}_{D,k}} \tag{5.79}$$

This factor helps to set a type of component (heat exchangers, turbines, pumps, etc.) straight, by means of finding the most efficient solution. This solution has the lowest specific expenses as a result of having both lowest exergy destruction ($c^{ED}_{P,k,A}$) and investment cost ($c^{Z}_{P,k,A}$) and, therefore, the minimum $c_{P,k}$ value (Figure 5.4).

In general terms, components with a low f-factor suggest that cost savings in the entire system might be achieved by improving the component efficiency, that is reducing the exergy destruction even if the capital investment for this component increases. Moreover, components with high value in this factor (>70%) suggest a decrease in the investment costs at the expense of its exergetic efficiency. In this thesis, a component is considered to have a low f-factor when this factor is lower than 30%, and to have a high f-factor when this factor is higher than 75%. From bibliography (reference [5]), only the following exergoeconomic factors as the most common in thermal systems are suggested: heat exchangers present usually f-factor values lower than 55%, compressors and turbines between 35 and 75%, and pumps above 70% . Nevertheless, in this thesis, a thermochemical system is studied, so these values cannot be properly taken as reference, normally because of material price discrepancies. Most sulfuric acid plant components have to be protected against acid corrosion and that increases severely its purchase costs.

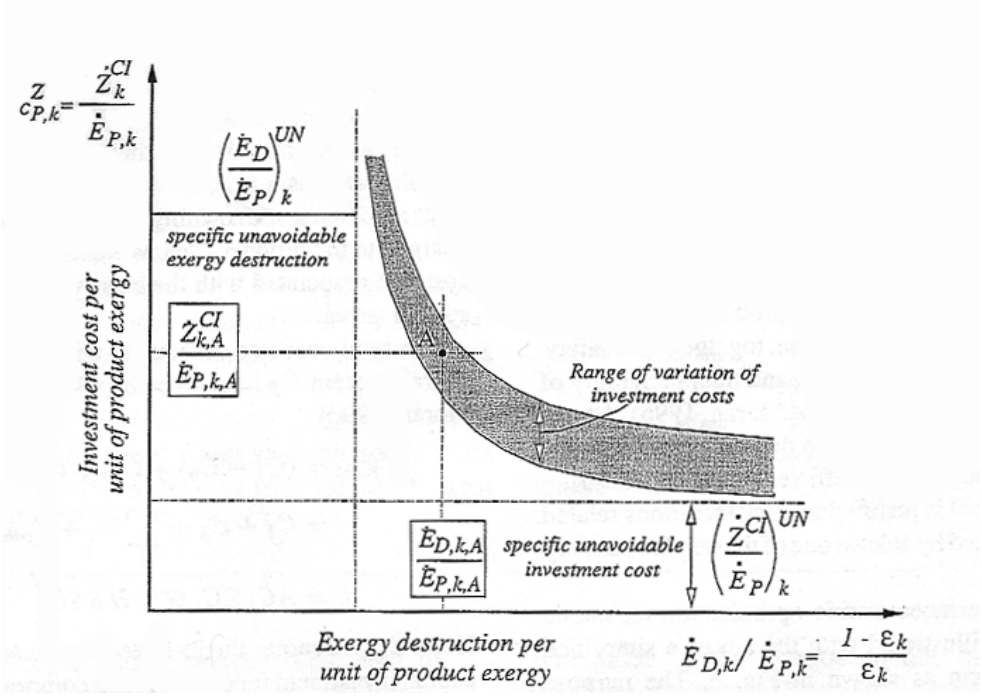


Figure 5.4: Relationship between investment cost and exergy destruction for the kth component of a thermal system [9]

5.4 Thermoeconomic Evaluation

A thermoeconomic evaluation consists basically of calculating for each system component the thermoeconomic variables introduced in the last section. Table 5.8 shows the results of such an evaluation. It should be remarked that in this table, exergy destruction rates and ratios, and cost rates associated with capital investment and maintenance are added to complete the understanding of the system. Summarizing, for the kth component it is calculated:

- Exergy destruction rates, $\dot{E}_{D,k}$
- Exergy destruction ratio, $y^*_{D,k}$
- $\dot{Z}$-costs
- Exergy destruction cost rate, $\dot{C}_{D,k}$
- Exergoeconomic factor f_k

In order to improve the cost effectiveness of the considered sulfuric acid plant, it is kept to the proceedings presented in bibliography by [5] and [9] used to improve a thermal system. This methodology recommends to follow the next steps:

1. Rank the components in order decreasingly using the sum $\dot{Z}_k + \dot{C}_{D,k}$

2. Consider design changes initially for the components for which the value of this sum is high.

3. Use the exergoeconomic factor f_k to identify the major cost source, that is $\dot{Z}$-costs or $\dot{C}_{D,k}$, and proceed as explained in 5.3.3:

    - a. If f_k is high, the cost effectiveness of the entire system might increase by reducing the capital investment for the kth component at the expense of its efficiency.
    - b. If f_k is low, the cost effectiveness of the entire system might increase by increasing the efficiency of the kth at the expense of a higher investment cost.

4. Improve the exergetic efficiency of a component if it has relatively large values of exergy destruction rate, exergy destruction ratio, or exergy loss ratio.

Table 5.8 shows all values needed to understand a thermoeconomic analysis in the reference system and suggests in which direction the variables and design of this system should change in order to improve its cost efficiency. The following analysis is limited itself to only comment the possible improvements, so the corresponding methodology is explained in next chapter more in detail.

5.4.1 Reference Case Evaluation

The absorbtion column presents the highest value of the sum $\dot{Z} + \dot{C}_D$, so this component is the most important from the thermoeconomic point of view. Nevertheless, the f-factor (48%) does not show anything relevant, but that the costs associated with the absorbtion are almost in the same proportion due to both investment and exergy destruction expenses. This fact added to that no reference information about which is the most common f-factor for such a component was found (see the exergoeconomic factor section) and that the sum $\dot{Z} + \dot{C}_D$ is not feasible to reduce (see Section 6.2.1) states that this component cannot be thermoeconomically improved within. Therefore, the only way to sink product costs is by reducing the expenses in upstream components. In the next chapter, this discussion is explained more in detail.

	$\mathbf{c}_F$ [€/GJ]	$\dot{Z}$ [€/h]	$\mathbf{c}_P$ [€/GJ]	$\dot{C}_D$ [€/h]	$\mathbf{y}_D^*$ [%]	$\dot{Z}+\dot{C}_D$ [€/h]	f [%]
Absorbtion column	70.6	103	138	113	12.1	215	48
Heat exchanger 2	31.5	158	52.5	18.7	4.5	177	96
Heat exchanger 1	6.29	112	10.5	21.4	25.9	134	84
Contact bed 2	20.9	79.7	32.2	3.23	1.18	82,9	97
Sulfur burner	0.75	45.3	3.85	4.19	42.5	49.5	92
Mixer 3	198	0.00	198	22.6	0.87	22.6	0.0
Compressor	44.7	10.2	102	4.38	0.75	14.6	73
Heat exchanger 3	0.18	10.4	12.5	0.16	6.40	10.6	99
Mixer 1	19.7	0.00	20.9	9.09	3.51	9.09	0.0
Contact bed 3	33.1	7.97	34.3	0.66	0.15	8.63	93
Contact bed 1	18.1	3.19	18.9	2.69	1.13	5.88	59
Mixer 2	32.5	0.00	33.1	4.64	1.08	4.64	0.0
Pump 1	44.69	0.00	0.00	0.00	0.00	0.00	0.0
Pump 2	44.69	0.00	0.00	0.00	0.00	0.00	0.0
Total		530		204		735	

Table 5.8: Thermoeconomic variables from the reference plant in order decreasingly, accordingly to the sum $\dot{Z}+\dot{C}_D$ (Intermediate case)

The next highest sum $\dot{Z} + \dot{C}_D$ is presented by the second heat exchanger. With a high f-factor (96%), this component reveals that the most of the costs are due to investment expenses, so its exergoeconmic efficiency might be improved by reducing its purchase cost. It is important to observe that the reduction of the product costs of this component leads also to a reduction of the product costs of the absorbtion column, since the cost rate $\dot{C}_9$, which is a part of the second heat exchanger product, correspond to the fuel costs of the absorber. Consequently, this reduction yields directly to a decrease in the exergy destruction expenses of this last component.

The first heat exchanger corresponds to the third highest sum of investment and exergy destruction costs. The f-factor presents a high value (84%) and therefore the methodology of improvement in this component is the same as in the second heat exchanger. This component is located at the beginning of the sulfuric acid process, so the reduction of its product costs might have a relevant positive influence in the subsequent component product costs and then, in the entire process from an exergoeconomic point of view.

Chapter 6

Thermoeconomic Optimization

In this chapter, the term optimization is understood as that variables configuration or design changes in the process under boundary conditions that lead to a decrease in the levelized cost of the system products [Equation (6.1)]. For that, the methodology used is based on the statements given in the thermoeconomic evaluation performed in Section 5.4, which basically indicate that the highest sums $\dot{Z} + \dot{C}_D$ among all plant components have to be mainly reduced. Additionally, process optimizations based on mathematical models are subject to study in further works.

$$Minimize \;\; \dot{C}_{P,tot} = \dot{C}_{F,tot} + \dot{Z}_{tot} \tag{6.1}$$

It should be remarked that the aim of Equation 6.1 is not to minimize the levelized specific product costs ($c_{P,tot}$) as in usual thermal systems optimizations, but the product cost rates ($\dot{C}_{P,tot}$). That happens because normally, in thermal systems, the amounts of energy to be supplied by the system in terms of generated electricity and vapor steam are fixed values, so minimizing the product cost rates with Equation (6.1), would minimize also the specific product costs. Nevertheless, in the reference plant, it is only specified the product amount of sulfuric acid (stream *12*), so the vapor generated is always subject to the plant configuration. For that reason, in this work, as a result of minimizing Equation (6.1), new plant configurations might lead to smaller amounts of steam than in the reference plant and consequently, the exergetic efficiency of the plant is reduced. In this case, the results are also of interest since even producing less steam, the selling price of the sulfuric acid might decrease. This fact is discussed at the end of the chapter.

6.1 Decision Variables and System Constrains

The *decision variables* are those independent variables which characterize the system and how the name states, its value might be changed in order to minimize the levelized costs of the system products. Moreover, it is considered that the steam is generated at the fixed pressures of 40 and 5 bar in the first and second heat exchangers, respectively. In this work, the sulfuric acid process is defined by the following decision variables with its corresponding system constrains:

- **Sulfur burner outlet temperature, $\mathbf{T}_2$.** From 1200 °C on, NO_x begins to be present in the mixture, so the maximum value allowed for T_2 should be close to 1200 °C. On the other hand, there is not a minimum restriction, but it should be taken into account that when T_2 diminishes, more atmospheric air is required in the combustion chamber [see Equation (2.2)].
- **First heat exchanger: Gas outlet (or first contact bed inlet) temperature, $\mathbf{T}_3$.** This temperature as well as the other contact bed inlet temperatures has a strong influence in the SO_2-SO_3 catalytic reaction. As explained in Section 1.2.1, the minimum and maximum temperatures for best operating conditions are pretty close. Consequently, in this thesis, this variable ranges from 400 to 500 °C. In the optimization, it should be consider the fact that for a fixed T_2 value, the higher T_3 is, the less vapor steam at fixed 40 bar is produced.
- **First contact bed outlet SO_3-concentration, $\mathbf{x}_{4,SO_3}$.** This variable is set according to the expected overall SO_2-degree of conversion at the first bed outlet (88.8%) which is related to the bed inlet temperature. Nevertheless, x_{4,SO_3} as well as the other contact beds outlet concentrations are considered parameters in this thesis, since the improvement of the system due to changes in the SO_2-SO_3 subsystem is subject to study in further works.
- **Second bed inlet temperature, $\mathbf{T}_5$.** As T_3, the value should range from 400 to 500 °C.
- **Second contact bed outlet SO_3-concentration, $\mathbf{x}_{6,SO_3}$.** As x_{4,SO_3}, this variable is considered a parameter and has a corresponding overall conversion degree of 99.3%.
- **Third bed inlet temperature, $\mathbf{T}_7$.** The higher the bed inlet temperature

is, the faster the catalytic reaction takes place and consequently, for a given inlet amount of SO_2 less catalyst is required leading to lower bed investment costs (first and second contact beds). On the other hand, the lower the bed inlet temperature is, the slower the reaction takes place and consequently, for the same given inlet amount of SO_2 more catalyst is required leading to higher bed investment costs. Nevertheless, a higher overall conversion can be reached. For that, in the third contact, a lower inlet temperature is chosen, since most of SO_2 is already converted into SO_3 yielding an overall conversion of 99.9%.

- **Third contact bed outlet SO_3-concentration, $\mathbf{x}_{8,SO_3}$.** As x_{4,SO_3} and x_{6,SO_3}, this variable is considered a parameter.
- **Second heat exchanger: Gas outlet temperature, $\mathbf{T}_9$.** This temperature cannot be lower than the temperature of the inlet water, which is a fixed parameter and has a value of 100 °C; otherwise the heat exchanger would enter into the so called *pinch zone*. From bibliography [4, 17], the suggested temperature ranges are [180-220]°C and [165-230 °C], respectively. In the thesis, the hottest suggested temperature is taken as the tolerable maximum, which has a value of 230 °C. As in the first heat exchanger, the higher the T_9 value is, the less vapor steam at fixed 5 bar is produced.
- **Absorber acid recycling mass stream, $\dot{m}_{13}$.** This variable basically helps to regulate the outlet temperature in the absorber, T_{10}, in harmony with the second and third heat exchanger outlet temperatures T_9 and T_{15}, respectively. That means for example that for T_9 and T_{10} fixed values, $\dot{m}_{13}$ might be increased only if T_{15} is also increased. This mass stream is an interesting variable because it leads to different trade-offs between the investment expenses generated by the absorber and the third heat exchanger.

  Figure 6.1 shows the recommended operating region in sulfuric acid packed absorbers, so each new value of $\dot{m}_{13}$ has to be validated by the given ranges. Values on the left side of the suggested limits represent the *dewetting region*, while values on the right side indicate liquid flooding. According to this, for the absorber design in the reference case (Table 2.3), the maximum limit of $\dot{m}_{13}$ equals to 205000 kg/h ($\dot{m}_{13,flood}$). Values slightly higher than $\dot{m}_{13,flood}$ brings the absorber in the region of flood. On the other hand, the minimum value is not limited by the suggested ranges, but by the highest allowed sulfuric acid

temperature of 65 °C, $T_{10,max}$. This temperature always depend on the values of T_9 and T_{15}, so for the reference case, the minimum permissible value of $\dot{m}_{13}$ corresponds to 50000 kg/h ($\dot{m}_{13,corr}$). Values slightly smaller than $\dot{m}_{13,corr}$ can cause damages in the absorber due to a higher acid temperature and thus a higher corrosivity.

For a fixed absorber operating point, the relation between $\dot{m}_{13}$ and the purchase cost of the absorber should be considered. That is, the investment prices sink when the volume of the tower also sinks (see Section 4.2.1). For that, the area should be smaller which implies that for a fixed gas velocity trough the column (1.4 m/s), the SO_3-containing mass stream should decrease. Consequently, in order to maintain the value of the liquid mass flow across the section, $\dot{m}_{13}$ has to be increased. These considerations cannot be used in order to optimize the system here because the bed outlet concentrations are taken as fixed parameters in this thesis.

- **Third heat exchanger: Liquid outlet temperature, T_{15}.** As explained before, this variable has to take into account the value of $\dot{m}_{13}$ in order to operate correctly in the absorbtion process. The maximum is set by $T_{10,max}$ and corresponds to 43 °C for the reference case; while the minimum is set by the inlet cooling water temperature, T_{31} (20 °C).
- **Compressor isentropic efficiency, η_{sc}.** This variable corresponds normally to a decision variable, but in this work it is treated as a fixed parameter.
- **Third heat exchanger: Water outlet temperature, T_{33}.** For a fixed heat duty in the third heat exchanger, the higher the value of T_{33} is, the less cooling water is needed, and thus less power in the second pump is required. Therefore, this variable pretends to be as high as possible, but always according to the following environmental regulation stated in this thesis: the cooling water must not be returned at temperatures higher than 23 °C. However, it should be considered that an increase in T_{33} involves an increase in the system exergy loss, so the best trade-off between required electricity for the second pump and exergy loss should be found.

It should be remarked that both pump's isentropic efficiency and outlet pressure are not considered decision variables, since its influence in the system product costs can be neglected (see Table 5.8). Table 6.1 summarizes all plant decision variables with

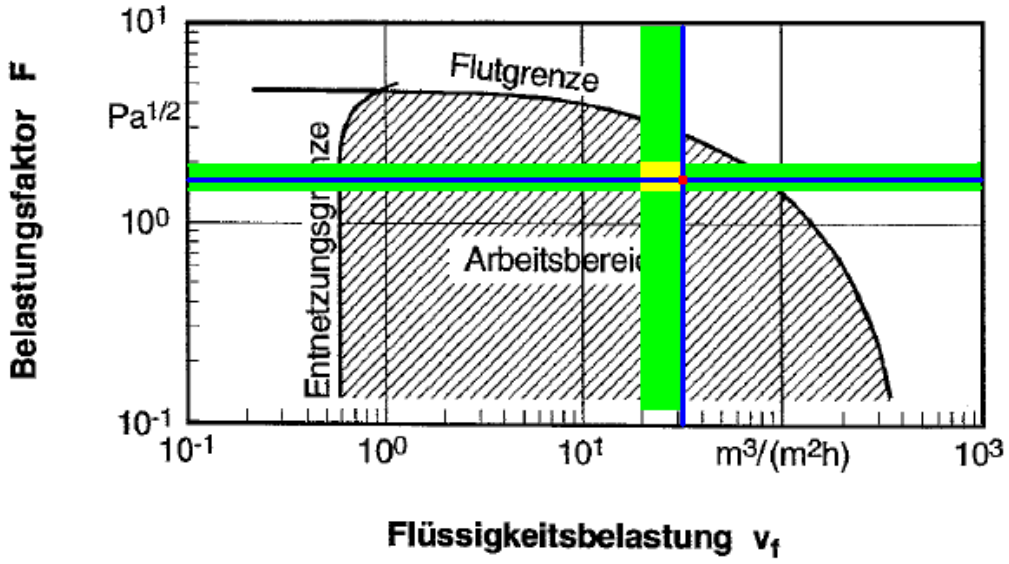


Figure 6.1: Operating area in packed towers. F and v_f refer to the *load factor* and the *volumetric liquid flow through the absorber*, respectively. The first is calculated by $v_g\sqrt{\rho_g}$, where v_g is the gas velocity and ρ_g the gas density; while the second is calculated by $\dot{V}_l/A_Q$, where $\dot{V}_l$ is the liquid volume flow's rate and A_Q the cross section of the column. The green color indicates the suggested operating ranges for sulfuric acid packed towers [31], so the yellow color represents the valid operating area. The red dot means the reference plant operating point.

its corresponding value constrains.

Decision Variable	**Constrains/Ranges**
Sulfur burner outlet temperature, T_2	$<$1200 °C
First heat exchanger: Gas outlet temperature, T_3	[400-500]°C
Second bed inlet temperature, T_5	[400-500]°C
Third bed inlet temperature, T_7	[350-500]°C
Second heat exchanger: Gas outlet temperature, T_9	[100-230]°C
Absorber acid recycling mass stream, $\dot{m}_{13}$	[50000-205000]kg/h
Third heat exchanger: Liquid outlet temperature, T_{15}	[20-23]°C

Table 6.1: Decision variables of the sulfuric acid plant in the initial case with its constrains and ranges

6.2 Possible Plant Optimizations

In this section, three improvements are performed in order to minimize the levelized costs of the plant products. The first improvement, *Improvement I*, is carried out by changing the values in the decision variables; while the others, *Improvement II and III*, consist basically on different plant designs.

6.2.1 Improvement I

By following the suggestions considered in the thermoeconomic analysis (Section 5.4), the high sum $\dot{Z} + \dot{C}_D$ in the absorber, as well as the investment costs from both first and second heat exchangers should be decreased.

The absorbtion column presents a f-factor of 48%, which is not neither a big nor a small percentage. Additionally, no references about usual f-factor for packed columns in the industry were found, so it is not clear whether the investment costs or the expenses associated with exergy destruction should be reduced. Thus, the most intuitive way of reducing the levelized sulfuric acid cost is by reducing the sum $\dot{Z} + \dot{C}_D$. On one hand, the investment costs might be reduced, but as explained in the last section (acid recycling mass stream definition), the purchase cost of the absorber depends on fixed parameters, so this term in the sum cannot be changed. On the other hand, the exergy destruction might be lowered by changing the decision variables T_9, $\dot{m}_{13}$, and T_{15}. The results shown in Figures 6.2, 6.3, and 6.4 conclude the following statements:

- The exergy destruction sinks when the second heat exchanger acid outlet temperature (T_9) also diminishes (Figure 6.2). Consequently, it causes an increase in the investment costs of the heat exchanger, which is opposed to the changes suggested by the thermoeconomic analysis. Even if this temperature is decreased, for a fixed value of m_{13} and T_{15}, the plant would suffer corrosion problems due to an increase in T_{10}. In that case, the only solution would be to cool the sulfuric acid at the absorber outlet by using a heat exchanger capable of operating with high corrosive loads (e.g. glass heat exchangers). In Appendix B.1 a possible solution is shown, where the third heat exchanger -made of proper material- is moved to the outlet of the absorber. The elevated prices of anticorrosive materials might increase the total price of the products,

though.

- The exergy destruction sinks when the acid reflux ratio ($\dot{m}_{13}$) also diminishes (Figure 6.3). Consequently, the acid outlet temperature T_{10} increases, so the absorber has to be cooled in order to avoid damages due to corrosion by lowering the temperature T_{15}. In that case, as shown in the next statement, the exergy destruction would increase again.
- The exergy destruction sinks when the third heat exchanger acid outlet temperature (T_{15}) also diminishes (Figure 6.4). Consequently, the acid outlet temperature T_{10} increases, so the absorber has to be cooled again in order to avoid damages due to corrosion by increasing the acid reflux ratio ($\dot{m}_{13}$). Therefore, as shown in the last statement, that would increase the exergy destruction again.

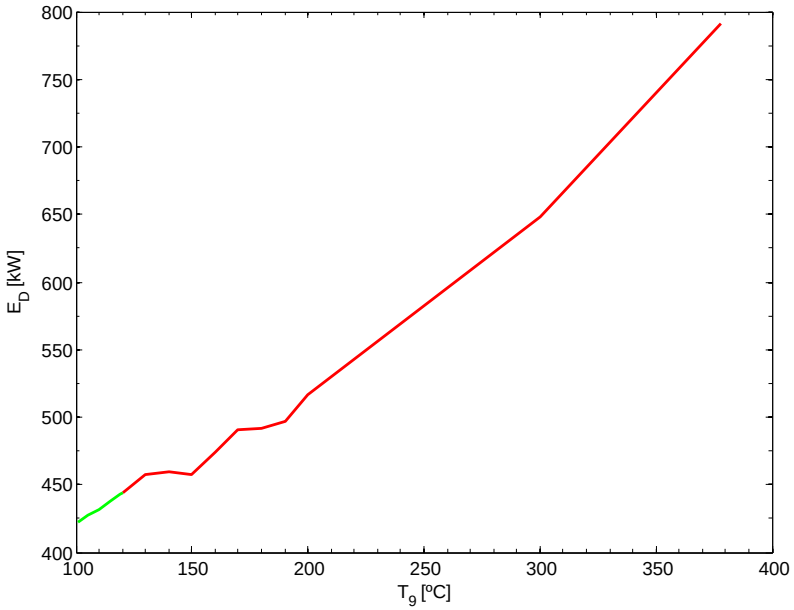


Figure 6.2: Exergy destruction in the absorber ($\dot{E}_{D,abs}$) v.s. Second heat exchanger acid outlet temperature (T_9), for $\dot{m}_{13}$ and T_{15} fixed values

Summarizing, a reduction in the exergy destruction of the absorber is not feasible. Moreover, it should be remarked that the percentage of the exergy that exits in relation with the exergy that enters into the absorber presents a high value of 98.9% [see Equation (6.2)], so all efforts to reduce the exergy destruction in this work are considered to be in vain. As concluded in Section 5.4, the only way to reduce the costs of the product sulfuric acid is by reducing the costs in upstream products, that

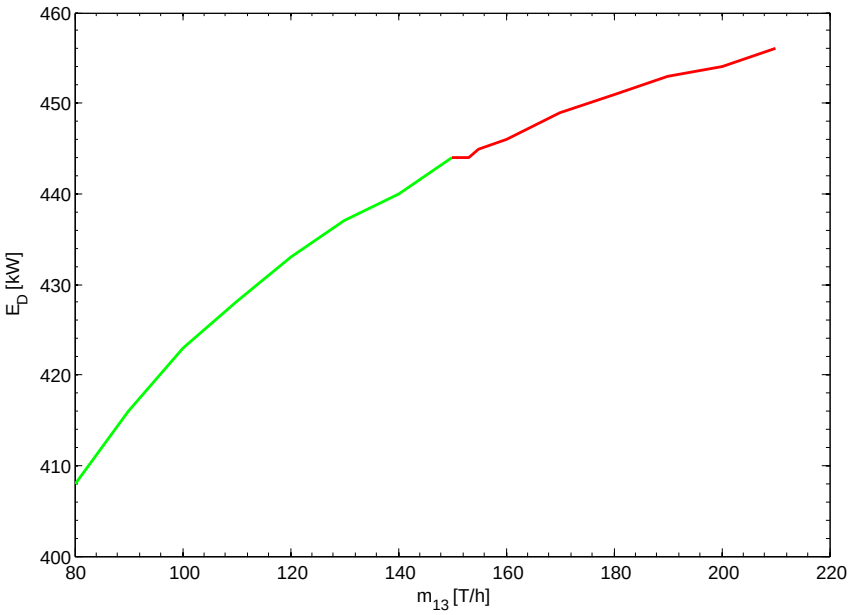


Figure 6.3: Exergy destruction in the absorber ($\dot{E}_{D,abs}$) v.s. Acid recycling mass stream ($\dot{m}_{13}$), for T_9 and T_{15} fixed values

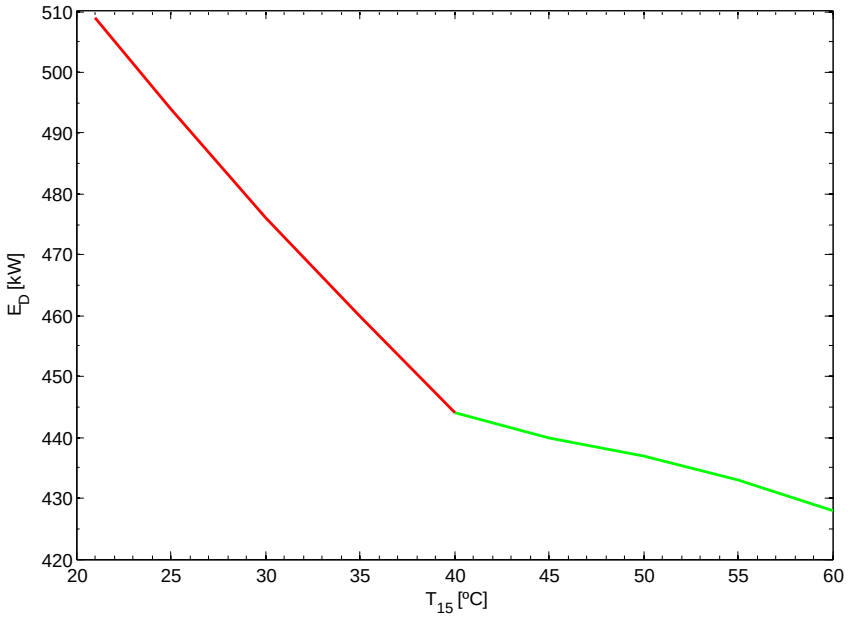


Figure 6.4: Exergy destruction in the absorber ($\dot{E}_{D,abs}$) v.s. Third heat exchanger acid outlet temperature (T_{15}), for T_9 and $\dot{m}_{13}$ fixed values

is in both first and second heat exchangers.

$$\frac{\dot{E}_{10}+\dot{E}_{16}}{\dot{E}_9+\dot{E}_{15}}\cdot 100 = \frac{39.0+0.04}{38.1+1.40} = 98.9\% \tag{6.2}$$

The investment cost of the first heat exchanger can be reduced by having a higher

temperature at the acid gas outlet T_3. On the other hand, an increase in this temperature leads to a major need of atmospheric air by means of cooling now a hotter gas, as well as a major electricity supply for the compressor. The influence of this implications in the levelized costs of the plant products should be studied through an *advanced exergy analysis* in further works [10].

As explained in the PEC calculations for heat exchangers (Section 4.2.1), this cost depends basically on the heat duty and the logarithmic mean temperature difference (LMTD) of the exchanger. Therefore, to reduce costs, the heat duty should decrease, while the LMTD should increase. That is achieved by increasing T_3 to 500 °C, which is the maximum tolerable temperature at the outlet of the first exchanger. Consequently, the heat duty diminishes down to 2749 kW (reduction of 11.6%) and the LMTD increases to 636 (increase of 12.7%), yielding a new purchase price of 523,515 mid-2008 euros (reduction of 14.8%). That shows that even if this component operates in the limit situation of exiting gas at 500 °C, it can only reduce in a 14.8% its purchase investment cost. That is considered a small change in comparison to heat exchangers operating in thermal systems, which are not subjected to so straight temperature operating ranges. Additionally, the fact that this heat exchanger is located highly upstream in the process reveals that small operating changes might present a remarkably influence in downstream components [10]. This feature can be studied by allowing changes in the hordes' configuration.

In the case of the second heat exchanger, the procedure is the same as in the first: the investment costs are reduced by bringing the outlet temperature T_9 to its upper limit (230 °C), so the heat duty diminishes to 985 kW (reduction of 29.4%) and the LMTD increases to 174 (increase of 104%), all together yielding a new purchase price of 430,363 mid-2008 euros (reduction of 50.4%). On the other hand, this operating change increases also the temperature at the outlet of the absorber (T_{10}), so the acid reflux ratio has to be set to 200000 kg/h and the temperature T_{15} to 38 °C in order to maintain T_{10} around 63 °C ($T_{10,max}$=65 °C) and not reaching the region of flood in the absorber.

The cooling in the absorber (T_{10}) can be regulated by changing the configurations of the second and third heat exchangers, as well as the absorber's reflux ratio ($\dot{m}_{13}$). That is, for a fixed second heat exchanger gas inlet temperature (T_8) and a required T_{10} value, the lower the cooling in the second heat exchanger is, the higher the

cooling through $\dot{m}_{13}$ and the third heat exchanger hast to be. Therefore, in order to reduce investment costs in the second and third heat exchanger, the cooling in the absorber should be performed by having as much reflux ratio as possible without crossing the limits given in Figure 6.1, so the dimensions of both heat exchangers can be smaller and the tower's height and diameter remain constant.

After finishing an exergy and an economic analysis according to the new plant configuration set by Improvement I, the next step consists on performing a thermoeconomic analysis. The results are shown in Table 6.2 only for the most important components from the thermoeconomic point of view.

	$\mathbf{c}_F$ [€/GJ]	$\dot{Z}$ [€/h]	$\mathbf{c}_P$ [€/GJ]	$\dot{C}_D$ [€/h]	$\mathbf{y}^*_D$ [%]	$\dot{Z}+\dot{C}_D$ [€/h]	f [%]
Absorbtion column	55.5	113	120	114	14.4	227	50
Heat exchanger 2	22.1	86.6	36.8	14.1	4.51	101	86
Heat exchanger 1	6.57	105	11.0	20.8	22.3	126	83
Contact bed 2	19.8	87.8	31.8	5.30	1.88	93,1	94
Sulfur burner	0.74	49.9	4.13	4.14	39.3	54.0	92
Total		484		200		684	

Table 6.2: Thermoeconomic variables decreasingly ordered according to the sum $\dot{Z}+\dot{C}_D$ for the Improvement I (Intermediate case)

This table reflects that the efforts to reduce the sum $\dot{Z}+\dot{C}_D$ in the absorber by means of decreasing the investment costs in the first and second heat exchanger were in vain, since its value is bigger than in the initial case (Table 5.8). The reason might be a mass stream increase in most of the plant components due to a higher need of atmospheric air, since now more air is needed to quench hotter temperatures at the first contact bed outlet, all together leading to both higher exergy destruction and investment costs in the absorber. In further studies, it would be interesting to extend the Improvement I to the possibility of having the first heat exchanger operating at the initial case conditions in order to prove this last statement. Nevertheless, the current system configuration reduces in a 6.9% the total sum $\dot{Z}+\dot{C}_D$ of the process compared to the reference case, so it is confirmed that the thermoeconomic efficiency of the plant has been improved.

The specific product costs for the sulfuric acid (intermediate case), and the generated vapor steam at 40 and 5 bar are respectively 68.9 (17.6), 2.28 (0.64), and

7.56 ct./kWh (1.57 ct./kg) (Appendix B.10). Furthermore, Table 6.3 shows the values for the favorable and unfavorable cases.

Thermoeconomic	**Favorable**	**Intermediate**	**Unfavorable**
H_2SO_4	15.3	17.6	21.1
Steam (40 bar)	0.55	0.64	0.77
Steam (5 bar)	1.35	1.57	1.89
Economic	**Favorable**	**Intermediate**	**Unfavorable**
H_2SO_4	7.60	10.2	14.1
Steam (40 bar)	4.60	4.60	4.60
Steam (5 bar)	3.40	3.40	3.40

Table 6.3: Product prices in cents of euro per kilogram of both thermoeconomic and economic analysis for the Improvement I

The total levelized costs of the products are calculated by summing the new values of the cost rate streams $\dot{C}_{12}$, $\dot{C}_{26}$, and $\dot{C}_{28}$ from Appendixes B.10, B.1, and B.2 [Equation (6.3)]. Furthermore, the comparison between the total revenue obtained through both economic and thermoeconomic analysis can be found in Appendix B.10.

$$\dot{C}_{P,I} = 454 + 26.5 + 23.6 = 504.1\ euros/h \quad (\dot{C}_{P,0} = 546.4\ euros/h) \tag{6.3}$$

It is also interesting to compare the exergetic efficiency between the new and the reference plant configurations. By using Equation (3.23), the exergetic efficiency of the current improvement is calculated with a value of 31.6% that in comparison with a value of 36.7% from the reference case, it indicates a reduction in the efficiency. This reduction basically happens due to a lower vapor steam generation in both first and second heat exchangers, as well as due to a major need of fuel, that is major atmospheric air and electricity in both compressor and pumps.

6.2.2 Improvement II

In Improvement I, the variables are set at their bounds in order to reduce the levelized costs of the products. In Improvement II, as well as in the next improvements,

it is gone through this limitations by means of changing the design of the plant. In this case, the second heat exchanger is eliminated from the plant in order to reduce investment cost and thus, increase the exergoeconomic efficiency of the process, so the absorbtion column is cooled only by the acid reflux ratio and by the third heat exchanger (Appendix B.2). The new results are shown in Table 6.4 for the most important components from the thermoeconomic point of view.

	$\mathbf{c}_F$ **[€/GJ]**	$\dot{Z}$ **[€/h]**	$\mathbf{c}_P$ **[€/GJ]**	$\dot{C}_D$ **[€/h]**	$\mathbf{y}^*_D$ **[%]**	$\dot{Z}+\dot{C}_D$ **[€/h]**	**f [%]**
Absorbtion column	40.0	122	106	127	21.4	249	49.0
Heat exchanger 1	7.49	134	12.5	25.5	23.2	159	84.0
Contact bed 2	24.5	94.8	38.0	3.79	1.05	98.6	96.2
Sulfur burner	0.81	53.9	4.46	4.50	38.1	58.0	92.3
Total		456		206		662	

Table 6.4: Thermoeconomic variables from the reference case decreasingly ordered, accordingly to the sum $\dot{Z}+\dot{C}_D$ for the Improvement II (Intermediate case)

The results are difficult to compare with the results obtained from the reference case and the first improvement, since the design of the plant has changed. The second heat exchanger was eliminated from the process, so now the total plant expenses ($\dot{Z}_{tot}$) has to be distributed into less components. That can be appreciated in the term $\dot{Z}$ of the Table 6.4, where apparently this value rates should be smaller but with the new cost distribution they are higher. The reason is that the total OAM costs have not changed, since they depend only on the number of plant workers (see Section 4.2.4), so even if the total PEC is reduced, the new $\dot{Z}_{tot}$ costs for each component are higher [see Equations (5.3) and (5.4)]. Moreover, the third heat exchanger presents a bigger heat duty than in the reference plant design, so its purchase cost also increases. In this cases, the best procedure to compare the different designs is in terms of the levelized product cost rates. Equation (6.4) shows that the total levelized cost rate of the plant products, $\dot{C}_{11}$ and $\dot{C}_{25}$, is smaller than the value obtained from the first improvement. Therefore, from the exergoeconomic point of view, this new design is more efficient than the first improvement.

$$\dot{C}_{P,II} = 438 + 34.2 = 472\ euros/h \quad (\dot{C}_{P,0} = 546.4\ euros/h) \tag{6.4}$$

The specific product costs for the sulfuric acid (intermediate case), and the generated vapor steam at 40 bar are 66.4 (17.0) and 2.60 ct./kWh (0.73 ct./kg), respectively

(Appendix B.11). The values for the favorable and unfavorable cases are shown in Appendix B.13.

The exergetic efficiency presents a value of 28.9%, which is lower than the efficiency from the last improvement, since no vapor steam at 5 bar is generated. Additionally, there is a major energy supply requirement in the second pump due to a higher heat duty in the second heat exchanger, so it makes the efficiency even lower.

6.2.3 Improvement III

This improvement tries a new plant design (Appendix B.3) where the second heat exchanger preheats water at 100 °C and 40 bar to its boiling point (250 °C), so this water is exclusively evaporated in the first heat exchanger. Even if the value of LMTD in the second heat exchanger is now smaller than in the reference plant, the heat duty is also reduced -no latent heat is generated- so a stronger reduction in the investment cost is achieved. In this case, the outlet temperature T_9 presents a value of 175 °C. This new design increases the purchase cost of the first heat exchanger due to a lower LMTD value: the temperature at the water inlet is higher than in both reference case and last improvements. Nevertheless, Table 5.8 shows that the second heat exchanger presents a higher sum $\dot{Z} + \dot{C}_D$, so the reduction in its investment cost might lead to a major reduction in the total levelized costs of the products at the expense of a higher first exchanger cost. Comparing to the reference plant, the increase and reduction in the investment cost of the first and second heat exchangers are 19.0 and 69.0% (Table 6.6), respectively.

Table 6.5 shows the results of a new thermoeconomic evaluation for the most important components from the thermoeconomic point of view.

	$\mathbf{c}_F$ [€/GJ]	$\dot{Z}$ [€/h]	$\mathbf{c}_P$ [€/GJ]	$\dot{C}_D$ [€/h]	$\mathbf{y}^*_D$ [%]	$\dot{Z}+\dot{C}_D$ [€/h]	f [%]
Absorbtion column	60.0	112	126	106	13.5	219	51.5
Heat exchanger 1	8.01	146	13.3	23.6	22.6	170	86.1
Contact bed 2	24.7	87.3	37.2	3.82	1.19	91.1	95.8
Heat exchanger 2	10.7	53.9	21.5	6.79	4.86	60.7	88.8
Sulfur burner	0.78	49.6	4.16	4.35	42.8	54.0	91.9
Total		486		191		677	

Table 6.5: Thermoeconomic variables from the reference plant decreasingly ordered, accordingly to the sum $\dot{Z}+\dot{C}_D$ for the Improvement III (Intermediate case)

By summing the levelized cost rates of the plant products, $\dot{C}_{12}$ and $\dot{C}_{25}$, is calculated a value of 503 euros/h [Equation (6.5)], which is quite similar to the value obtained in the first improvement (504 euros/h). On the other hand, the exergetic efficiency is increased to a value of 36.9%.

It should be noticed that this design achieves a reduction in the levelized costs of the plant products close to the first improvement, but having an efficiency similar to the reference case, which is the highest efficiency among the suggested improvements. Therefore, it is stated that this improvement is more effective than Improvement I, since the exergetic efficiency and the levelized costs compared to the reference case are more favorable at the same time.

$$\dot{C}_{P,III} = 447 + 55.2 = 503\ euros/h \quad (\dot{C}_{P,0} = 546.4\ euros/h) \tag{6.5}$$

This new design basically shows how to increase the plant exergetic efficiency at the same time that the total investment cost is reduced for a fixed steam pressure of 40 bar, which is considered a system parameter. As shown in the first improvement, the levelized costs could be reduced even more by increasing the acid temperature T_9 in the second heat exchanger. This is only possible if the outlet temperature T_3 of the first heat exchanger increases or the pressure parameter (40 bar) decreases, since in this plant design T_9 is inversely proportional to the cooling water that has to be evaporated later, and therefore less water would be required in the second heat exchanger. Favorably, that differs from Improvement I in the fact that from the beginning the total levelized costs of the products are lower than in the reference case, so an increase of T_9 would reduce such costs more than in the first improvement. On the other hand, the exergetic efficiency might be lower.

Additionally, a parametrical study reveals that for a pressure of 30 bar, the total levelized costs and the exergetic efficiency decrease to a value of 497 euros/h and 34.8%, respectively; while at 50 bar, they increase to 530 euros/h and 38.7%.

The specific product costs for the sulfuric acid (intermediate case), and the generated vapor steam at 40 bar are 67.9 (17.3) and 3.10 ct./kWh (0.87 ct./kg), respectively (Appendix B.12). The values for the favorable and unfavorable cases are shown in Appendix B.14.

6.3 Optimization Summary and Conclusions

After evaluating Improvements I, II, and III presented in the last section regarding to the reference case, the following statements are concluded:

- Improvement I states that when all plant decision variables are set to its most favorable values (Table 6.6), from a thermoeconomic viewpoint, the TRR_L is only reduced in a 7.72% (Table 6.7). Moreover, the exergetic efficiency decreases due to a reduced production of vapor steam.

  The thermoeconomic evaluation reveals that the specific price of the sulfuric acid has decreased regarding to the price in the reference case, that is, now to produce 1 kg/h of sulfuric acid is cheaper. On the other hand, the selling price of the sulfuric acid increases, since the amount of total annual revenue solved by the sale of steam has decreased (Table 6.8).

  This improvement concludes that in order to improve the exergoeconomic efficiency of the plant, new plant designs has to be taken into account.

- Improvement II states that from all the improvements evaluated in this thesis, the best solution from the thermoeconomic viewpoint is to eliminate the second heat exchanger from the process: the TRR_L is reduced by 13.6%. Nevertheless, this new configuration leads to the lowest exergetic efficiency among the reference case and the other possible improvements (Table 6.7).

  Regarding to the product costs, the sulfuric acid presents a cheaper manufacture value, but its selling price is slightly lower than in the reference case, though. That happens due to the fact that a less amount of steam is produced in comparison with the reference case, so the selling price of the sulfuric acid

cannot decrease significantly. Nevertheless, the capital reduction in this improvement is major enough to counteract a less income due to the sale of steam and thus, the selling price of the sulfuric acid is lower than in the reference plant and in the first improvement (Table 6.8).

This improvement concludes that despite this improvement presents the lowest overall exergetic efficiency, it is the best solution from the thermoeconomic point of view.

- Improvement III states that by preheating water in the second heat exchanger and evaporating the same water in the first, the exergetic efficiency of the plant is close to the value of the initial plant design, but now presenting a reduction in the total annual requirement TRR_L close to the first improvement. Moreover, the selling price of the sulfuric acid due to both TRR_L reduction and slightly increase in steam production regarding to the reference case is the most competitive (8.17 ct.€/kg).

	$\mathbf{T_3}$ [°C]	$\mathbf{T_9}$ [°C]	$\mathbf{T_{15}}$ [°C]	$\dot{m}_{13}$ [T/h]	$\mathbf{PEC}_{HX_1}$ [th.€]	$\mathbf{PEC}_{HX_2}$ [th.€]
Reference	400	120	40	150	615	867
Improvement I	500	230	38	200	523	430
Improvement II	400	380[1]	33[1]	205[1]	615	0
Improvement III (40)	400	174	40	175	731	269
Improvement III (30)	400	205	40	187	709	226
Improvement III (50)	400	147	40	162	909	391

Table 6.6: Decision variables and purchase costs of the first and second heat exchanger for the reference plant and possible improvements (Intermediate cases); [1]In the Improvement II, T_9, T_{15}, and m_{13} correspond with T_8, T_{14}, and m_{12}, respectively

	$\mathbf{TRR}_L$ [th.€/year]	Reduction [%]	Ψ [%]	Steam [MWh/year]
Reference	4,785	-	36.7	15,395
Improvement I	4,416	7.72	31.6	12,911
Improvement II	4,135	13.6	28.9	11,524
Improvement III (40)	4,403	7.99	36.8	15,612
Improvement III (30)	*4,354*	*9.01*	*34.8*	*14,549*
Improvement III (50)	*4,642*	*3.0*	*38.7*	*16,554*

Table 6.7: Results for the reference case and possible improvements: levelized total required revenue, TRR_L; reduction of the TRR_L regarding to the reference plant; plant exergetic efficiency; and annual exergy from the total generated steam (Intermediate cases)

	THERMOECONOMIC			ECONOMIC				
	H_2SO_4 [%]	Steam [%]	H_2SO_4 [ct.€/kg]	Steam [ct.€/kg]	H_2SO_4 [%]	Steam [%]	H_2SO_4 [ct.€/kg]	Steam [ct.€/kg]
Reference (40/5)	86	14	18.2	0.61/2.24	47	53	10.0	4.60/3.40
Improvement I (40/5)	90	10	17.6	0.64/1.57	52	48	10.2	4.60/3.40
Improvement II (40)	93	7	17.0	0.73	54	46	9.95	4.60
Improvement III (40)	89	11	17.3	0.87	42	58	8.17	4.60
Improvement III (30)	90	10	17.3	0.83	45	55	8.72	4.46
Improvement III (50)	87	13	17.8	1.06	42	58	8.54	4.70

Table 6.8: Comparison between both thermoeconomic and economic analysis for the reference case and possible improvements through the percentages of the revenue obtained by the sale of sulfuric acid and steam regarding to the total required revenue (TRR_L), as well as the specific cost of the sulfuric acid from both thermoeconomic and economic analysis (Intermediate cases)

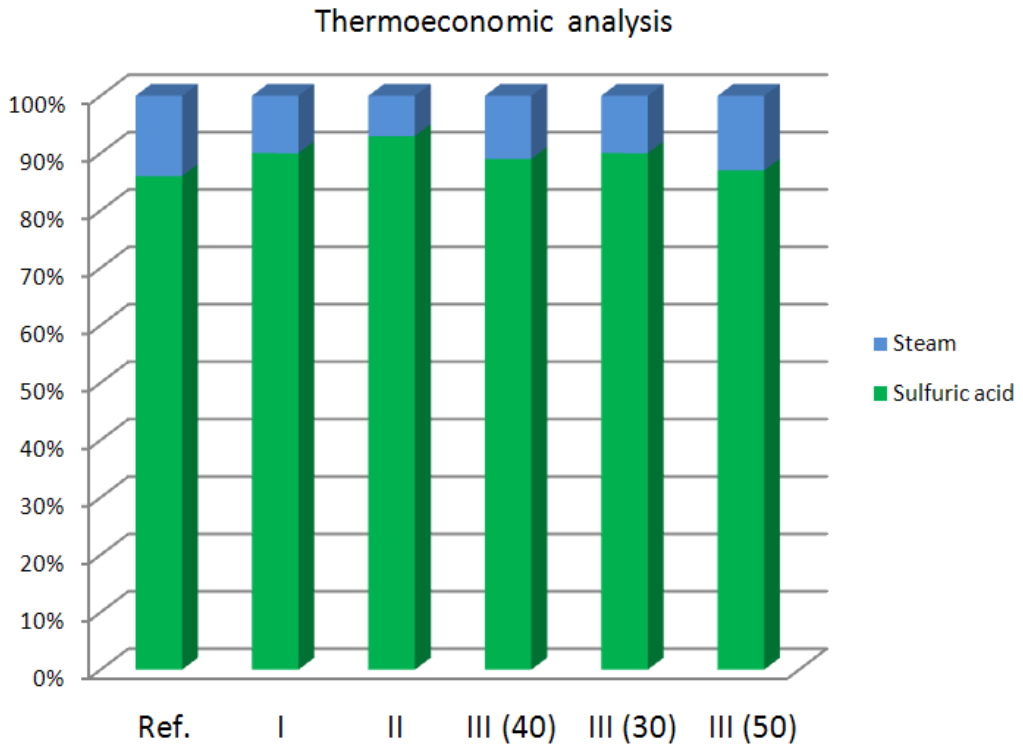


Figure 6.5: Percentages of the annual revenue obtained by the sale of sulfuric acid and steam regarding to the TRR_L (Thermoeconomic analysis)

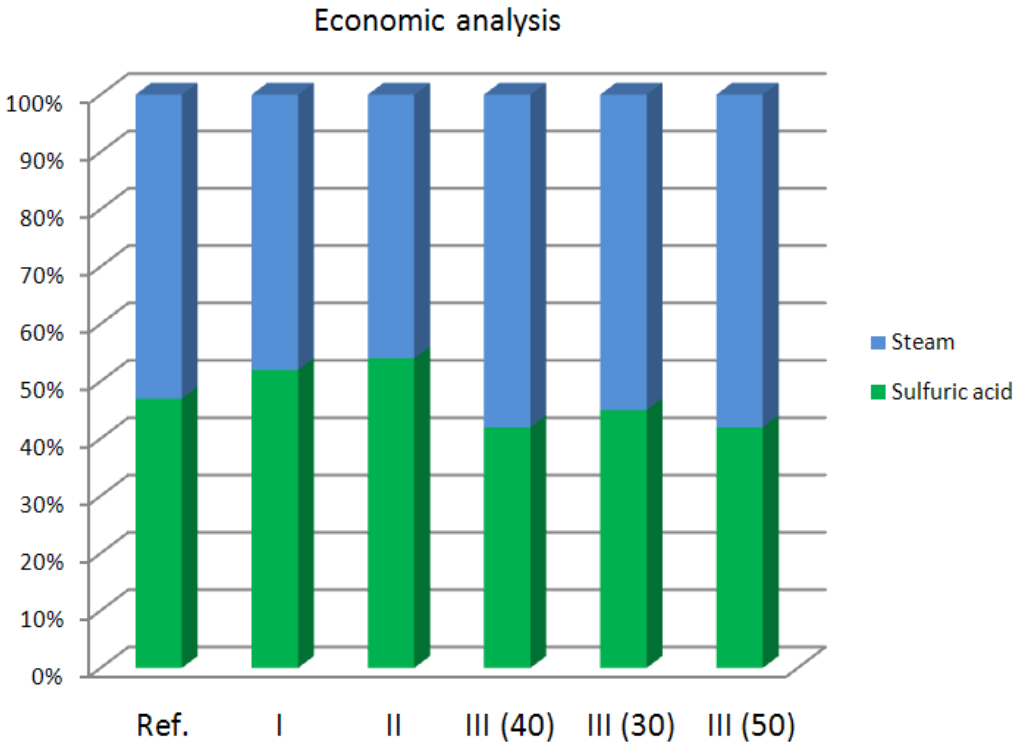


Figure 6.6: Percentages of the annual revenue obtained by the sale of sulfuric acid and steam regarding to the TRR_L (Economic analysis)

Chapter 7

Conclusions

The process studied in this work consists of a sulfuric acid plant of the wet-catalysis type. Consequently, the cooling in the catalysis process can be performed by quenching merely the sulfurous gases with atmospheric air. This fact reduces all expenses related to the drying machinery, since in a wet process the chemical reactions can be carried out in presence of liquid water. Additionally, the sulfuric acid is produced by absorbtion and not by condensation, as it normally happens in an ordinary wet process (e.g. Haldor Topsoe [26, 15, 14]), so high monetary expenditures due to corrosion-proof materials in such a process are avoided. On the other hand, these processes can lead to sulfuric acid concentrations higher than 78 wt% [26, 15, 14], while in a normal contact process a double absorbtion system would be needed. In this work, the considered process presents a concentration requirement of 78 wt% for the product sulfuric acid, though. Therefore, it can be said that this process has the advantages of both wet catalysis process (quench-cooling in the catalysis) and normal contact process (production of sulfuric acid by absorbtion).

Furthermore, it should be commented that a sulfuric acid plant by absorbtion needs to cool the sulfur trioxide gases before they enter into the absorbtion column leading to additional costs due to the purchase of a heat exchanger in comparison with a process by condensation. Nevertheless, this heat exchanger offers the possibility to produce more vapor steam, so the overall efficiency of the plant increases. In further studies, it would be interesting to compare the reference plant of this thesis (by absorbtion) with the same plant but by condensation.

The reference process is studied according to some simplifications: in the combustion chamber, the sulfur trioxide and the sulfuric acid are treated as inert gases,

as well as the NO_x emissions are not considered; the formation of sulfuric acid in the catalysis model is not taken into account; and the problem of the acid mist formation along the different stages of the process is not treated. In further studies, these simplifications and the fact that it would be interesting to perform sensitivity analysis related to some system variables (e.g. the amount of hydrogen sulfide at the entrance of the plant, and both NO_x and stack gas emissions) should be fulfilled in order to understand better the process' behavior and to obtain a more accurate overview of the reference plant.

For the exergy analysis, the activity coefficients of both water and sulfuric acid in a liquid mixture are calculated using the concept of the excess free enthalpy (g^E) (Section 3.2.2). The results confirm that when theses substances present molar fractions in a range of approximately 30 and 50% H_2SO_4 (Figure 3.5), their activity coefficients present the lowest values of the activity model ($<$0.1). That is, the strongest activity between both components. Nevertheless, these results should be compared with another activity coefficient calculation methodologies (e.g. through *phase equilibrium*) in further studies. Additionally, the activity coefficient of the SO_3 should be calculated, since the activity of this component in a liquid mixture in the presence of water is not avoidable [19, 32]. Despite that there are no streams in the process which contain both water and SO_3 in a liquid mixture, the calculation of the chemical exergy is performed at environmental conditions (T_o, p_o), so the phase of a stream could change from gas to liquid (see Section 3.4).

The exergy destruction of each system component calculated through an exergy balance is compared with the destruction calculated through the entropy generation concept. This comparison states the accuracy of CHEMEX -an add-on tool designed in this thesis for the exergy calculation in CHEMCAD- in relation with the electrolyte model used in the simulation (NRTL model), which takes into account the activities among all system components. The results show that, apart from the errors in the first pump (see Section 3.4), the highest relative errors are located in the first contact bed and the absorbtion column with a value of 10.6 and 9.69%, respectively (Table 3.4). The reason is basically that the activity coefficient of SO_3 is not taken into account in the calculation of the chemical exergy, since both components present a significant difference between the input and the output

components. For the first contact bed, this difference is stated by the input/output relation SO_2/SO_3, while in the absorbtion column by the relation SO_3/H_2SO_4.

The plant's overall efficiency presents a value of 36.7% which is lower than the efficiency of a similar plant from bibliography with a value of 47.2% (Section 3.5.1). This comparison is not definitive, but a general overview of the efficiency in wet-catalysis processes by absorbtion, since the components of both plants are not the same. The principal reason might be the use of different types of heat exchangers: gas/gas and liquid/air heat exchangers, as well as the use of an economizer in the plant with higher efficiency. In addition, the steam is produced in the second heat exchanger as in the first at 50 bar, a fact that from the thermoeconomic evaluation performed in this thesis concludes to be a solution that increases the overall efficiency of the plant (Table 6.7). Nevertheless, it is not the best solution from a thermoeconomic viewpoint (Section 6.3).

In Section 3.5.1, the exergy efficiency of the overall plant is calculated according to the fact that in a thermochemical system, as opposed to thermal system, the exergy efficiency definitions are neither found in bibliography nor are obvious to define. That happens with an heat exchanger that cools the main product but also produces steam (heat exchangers with two products: HX1 and HX2) and with the absorbtion column. In further studies, these efficiencies should be calculated.

The exergy destruction and exergy loss ratios of the overall plant present values of 57% and 6.1%, respectively (Section 3.5). In further studies, it would be interesting to set the ambient temperature to 20 instead of 25 °C; that is, the lowest temperatures among all system stream temperatures. In that case, the exergy losses from stream *16* (stack gases) would increase; on the other hand, the water from the third heat exchanger could be recycled in a closed water circuit, where a fourth heat exchanger would decrease its temperature to 20 °C yielding zero exergy losses according to Equation (3.13). Moreover, the industrial impact in the natural environment would be decreased, since now no water at 23 °C is wasted into the see.

In the economic analysis, the main problem is related to the uncertainty in the cost data. Some parameters such as the labor positions for operating and maintenance, and the average labor rate (euros/h) are difficult to determine, since they can be barely found in bibliography. The inflation rate and the capacity factor of the

plant are also parameters that even if they can be calculated, they are still approximations. According to the methodology used in this thesis, these parameters do not have a strong influence on the PEC. Therefore, all efforts of the economic analysis should be focused on an accurate PEC calculation. Nevertheless, assuming that this thesis only pretends to be an introduction to the optimization of sulfuric acid plants through the exergoeconomic method, the purchase prices of all plant's main equipment (e.g. compressor, sulfur burner, absorbtion tower, etc.) are approached by means of cost functions that are not accurate enough; for example, in the PEC calculation of the second (72.5 psi) and third heat exchanger (16 psi), the operating pressure is set to 150 psi due to Matches' web site limitations [2] (full vacuum, 150, 300, 450, 600, 900 psi), which leads to higher costs. In further works, the PEC should not be approached by general nature costing curves, but rather by original industry prices from similar plant components that later have to be recalculated by means of the component's capacity (see Section 4.2.1). The PEC of the absorbtion column is the only purchase cost calculated through an industry price by means of the total volume of the tower (m^3). On the other hand, the chemical companies are not interested in giving such prices due to the market competence, which is a fact that makes it even more difficult to gather this type of information. Therefore, it would be also interesting to define PEC functions for every system component in relation to its corresponding capacity variable (e.g. the heat exchange surface area in the case of heat exchangers or the tower volume in the case of the absorbtion column) and to additional parameters such us the type of material or the component operating pressure. That would lead to an analytical system optimization.

Moreover, it is important to remark that in any cost estimation, it is frequently possible to commit either underestimation or overestimation errors. For this reason, the total capital investment of the plant is calculated according to three possible cases (favorable, intermediate, and unfavorable) in terms of a solution range: [11,727; 23,949] with an intermediate value of 16,626 rounded thousand euros (mid-2008) (Section 4.3). Thus, the most favorable case (11,727) underestimates, while the most unfavorable (23,949) overestimates all plant costs. In order to verify these calculations, it is useful to calculate the TCI using the Lang factor [Equation (4.20)] yielding a value of 13,759 rounded thousand euros (mid-2008) which is located between the favorable and intermediate case. Considering the fact that this calculation

uses only the PCI to estimate the total costs of the plant and the inaccuracy in the calculation of the the solution range, it can be said that the results are quite satisfactory.

At the end of the economic analysis, the price at which the sulfuric acid should be sold in order to obtain an specific annual income (TRR_L) is calculated by fixing an annual selling price of the steam. Even that this last price is taken from bibliography [5], it is converted from dollar to euros, and it is escalated to the current year (2008), the selling price of the sulfuric acid presents a value of 7.0, 14.9, and 10.0 ct.euro/kg for the favorable, unfavorable, and intermediate case, respectively (see Section 4.4). Consequently, assuming an standard selling price for the sulfuric acid of 7.3 ct.euro/kg (Chemical Market Reporter, Section 4.4) and regarding to the fact that the price obtained in this thesis is the result of many simplifications and costing approaches, it can be said that the results are quite satisfactory. It has to be taken into account the fact that the price reported by the Chemical Market Reporter is only a general price and it does not distinguish between plants which produce sulfuric acid by means of pure sulfur and plants that use another type of sulfurous substance such in the considered process (H_2S). In the first case, the sulfur concentration in the plant streams is higher than in the second type of plants, so for the same amount of entering sulfurous stream into the plant, more sulfuric acid is produced, apparently leading to lower sulfuric acid prices [see Equation (4.44)]. Additionally, it is interesting to notice that the standard price of 7.3 ct.euro/kg is located between the calculated prices for the favorable and the intermediate case. This fact states that if the selling price of the sulfuric acid would have been estimated by means of the TCI calculated by the Lang factor, this price would be even closer to the standard price.

Regarding to the thermoeconomic analysis, the *real* prices of the product sulfuric acid and steams at 50 bar and 5 bar are calculated yielding 18.21, 0.61, and 2.24 ct.euro/kg, respectively (Tables 5.5 and 5.6). These values differ from the prices obtained through an economic analysis in a way that the *real* price of the sulfuric acid is higher and the prices of the steam are lower. That happens due to the fact that in the thermoeconomic analysis the sulfurous stream passes through many plant components before becoming the product sulfuric acid 78 wt.%, carry-

ing consequently a significant part of the plant costs in comparison with the steam. Another reason is the use of the α-factor in the auxiliary equations of the first and second heat exchangers (α=0.6). This factor could be set in a way that would yield the same product steam values for both thermoeconomic and economic analysis, but as explained in Section 5.2 it is set to a value that the sulfuric acid carries the most of the plant costs. On the other hand, in the economic analysis, the selling price of the steam is set by market prices (4.60 and 3.60 ct.euro/kg), which are higher than the prices approached by the auxiliary equations in the thermoeconomic analysis, leading to a lower selling price of the sulfuric acid (10.0 ct.euro/kg) and making possible the economic profitability of the plant. In this thesis, it is assumed that both sulfuric acid and steam products are totally sold, so even if the selling of sulfuric acid is loss-making, the total revenue requirement is achieved with the selling of the total amount of generated steam.

The fuel and product definitions of some components such as the absorber (Table 5.7) or the auxiliary equations for the first and second heat exchangers are examples of costing balances which were not found in bibliography, so its definitions are just an initial approach by applying the guidelines given in [5]. In further works they should be studied more carefully. Moreover, it should be taken into account that the exergy losses from the absorbtion column and from the third heat exchanger could be costed in a different way leading to different results; that is, different prices for the plant products.

In this work, the f-factor (Section 5.3.3) is a thermoeconomic variable which only indicates wether the investment cost of a specific component should be increased or decreased on the basis of its value in order to increase the economic efficiency of the plant. The problem is that a precise value for this variable in the case of a thermochemical systems is not known, since the values given in bibliography ([5]) are only valid for thermic systems. That happens due to the use of corrosion-proof materials in thermochemical systems. Therefore, the calculation of the f-factor for the most typical components in a thermochemical plant could be the subject of a new thesis.

The results of the thermoeconomic analysis shows that the absorbtion column is the component with the highest sum $\dot{Z} + \dot{C}_D$ (Table 5.8), so from a thermoeconomic viewpoint it is the most important component. The main reason is based on the fact

that this component presents a high purchase cost and it is located at the end of the process. Nevertheless, this component could not be improved neither by reducing its investment cost nor by reducing its exergy destruction rate (Section 5.4), but by improving upstream components such as the second heat exchanger. It would be interesting to study more carefully the thermoeconomic interactions between the different plant components; that is, how the thermoeconomic improvement of one component could improve downstream components. This phenomenon is an actual discussion topic in the subject of thermoeconomics and it is reviewed in the so called *advanced exergy analysis* [10]. The next two more important components from the thermoeconomic viewpoint are the first and second heat exchangers due to its elevated investment cost.

In the optimization, three possible new plant designs are studied in order to reduce the TRR_L: the first consists only of a new value assignation in some of the plant decision variables, while the second and the third consists of a new rearrangement of the components. The results show that the most efficient option from the thermoeconomic point of view is the second design, which eliminates the second heat exchanger, leading to a TRR_L reduction of 13.6% and reducing the *real* price of the sulfuric acid to a value of 17.0 ct.euro/kg. On the other hand, this design decreases the efficiency of the plant (28.9%) and does not reduce significantly the selling price of the sulfuric acid (9.95 ct.euro/kg). Additionally, it should be remarked that even having one less component in the plant (HX2) the $\dot{Z}$-costs corresponding to this third improvement are higher than in the reference plant. That happens due to the fact that these costs are calculated by means of the OAM-costs (Working capital, Section 4.2.4), which depend basically on the number of workers in the plant (Table 4.3). That means that even if there is one component less, the number of workers remain constant and thus, the OAM-costs too, instead of decreasing. In further works, these costs should taken into account the fact of operating with less or more components regarding to the reference plant, for example by using a factor.

The third design is interesting to comment, since for the case of 40 bar it presents the lowest selling price of the sulfuric acid (8.18 ct.euro/kg) and a slightly higher plant efficiency in comparison with the reference case (36.8%). This design is based on the use of the second heat exchanger as economizer so all the evaporation is

carried out in the first heat exchanger. It is observed that for the case of generating steam at 50 bar, the overall plant efficiency presents the highest value (38.7%), but the reduction of the TRR_L is small (3.0%). Therefore, it can be said that a way for increasing the efficiency of the plant is by generating steam with the use of the second heat exchanger as economizer and at a high steam pressure.

For further studies, it could be interesting to set the total amount of generated steam as a parameter and at a specific vapor pressure, as well as establishing the selling price of the sulfuric acid instead the TRR_L as the main objective of the optimization. These changes would lead to a more concrete solution.

The results of the termoeconomic analyses for the seceach improvement reveal that the new $\dot{Z}$-costs of the components are higher than in the reference case (Tables 5.8, 6.2, 6.4, and 6.5)

Bibliography

[1] Germany inflation rate (consumer prices). `http://www.indexmundi.com/germany/inflation_rate_(consumer_prices).html`.

[2] Matches' process equipment cost estimates. `http://www.matche.com/EquipCost/index.htm`.

[3] *VDI-Wärmeatlas*. Springer, 2006.

[4] *Ullmann's Encyclopedia of Industrial Chemistry, Sulfur Acid and Sulfur Trioxide*. Wiley, 2007.

[5] Michael Moran Adrian Bejan, George Tsatsaronis. *Thermal design and optimization*. Wiley, 1996.

[6] Joachim Ahrendts. Die exergie chemisch reaktionsfähiger systeme, 1977.

[7] L. B. Evans Chau-Chyun Chen. *A Local Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems*. AIChE Journal, March 1986.

[8] Hans Gaensslen. Abgekürtzes verfahren zur vorkalkulation der investitions- und produktionskosten von anlagen der organich-chemischen grundstoff-industrie mit hilfe thermischer kenngrössen, 1983.

[9] Frank Cziesla George Tsatsaronis. Thermoeconomics, 2002.

[10] Tatiana Morosuk George Tsatsaronis. Design improvement of an energy conversion system based on advanced exergy analysis, 2007.

[11] Kenneth M. Guthrie. *Process Plant Estimating Evaluation and Control*. Craftsman Book Company of America, 1974.

[12] Eric C. Guyer. *Handbook of Applied Thermal Design.* McGraw-Hill, March 1989.

[13] Frank R. Steward Jan Szargut, David R. Morris. *Exergy analysis of thermal, chemical, and metallurgical processes.* Hemisphere Publishing Corporation, 1988.

[14] Frands E. Jensen Jens K. Laursen. Wsa - meeting industry demands, Sep-Oct 2007.

[15] Haldor Topse Jens Kristen Laursen. Wsa - the process principles, Aug 2007.

[16] Ernest J. Henley Junior D. Seader. *Separation process principles.* Wiley, 2006.

[17] Kirk-Othmer. *Encyclopedia of Chemical Technology, Vol.23.* Wiley, 1997.

[18] Tadeusz J. Kotas. *The Exergy Method of Thermal Plant Analysis.* Butterworths, 1985.

[19] Heinrich Lennartz. Experimentelle untersuchungen zum dampf-flüssigkeits-gleichgewicht des systems h_2o+h_2o_4, 1980.

[20] Howard N. Shapiro Michael J. Moran. *Fundamentals of Engineering Thermodynamics.* Wiley, 2007.

[21] Ingo Müller. *Grundzüge der Thermodynamik.* Springer, 2001.

[22] Rober H. Perry. *Perry's chemical engineers' handbook.* Springer, 2001.

[23] Mario Schembra. Daten und methoden zur vorkalkulation des anlagekapitalbedarfs von chemieanlagen, 1992.

[24] Jan C. Schöneberger. Dokumentation zur vermessung des schwefelsäurekatalysators o4-115, 2008.

[25] Marshall Sittig. *Sulfuric Acid Manufacture and effluent control.* Chemical Process Review, Nr. 55, 1971.

[26] Haldor Topse. Wsa - flexible sulphur management.

[27] Richard Turton. *Analysis, Synthesis, and Design of Chemical Processes.* Prentice Hall, 2002.

[28] Bruno Waeser. *Die Schwefelsäurefabrikation.* Vieweg, 1961.

[29] Young I. Cho Warren M. Rohsenow, James P. Harnett. *Handbook of Heat Transfer.* McGraw-Hill, March 1998.

[30] James R. West Werner W. Duecker. *The Manufacture of SULFURIC ACID.* Reinhold Publishing Corporation, 1959.

[31] Winnacker/Küchler. *Chemische Technik: Prozesse und Produkte.* Wiley, 2005.

[32] Günter Wozny. Linkphasengleichgewichte starker elektrolyte aus dampfdruckmessungen und deren anwendung zur auslegung von trennkolonnen bei thermochemischen wasserzersetzungsprozessen, 1979.

Appendices

Appendix A

A.1 Interests During Plant Operation (ROI)

A.1.1 Favorable Case

	Common Equity				Preferred Stock			Debt		
Year	BBY	BD	RCEAF	ROI	BBY	BD	ROI	BBY	BD	ROI
2012	4,412	179	26	662	1,891	95	221	6,303	315	630
2013	4,208	179	26	631	1,796	95	210	5,988	315	599
2014	4,004	179	26	601	1,702	95	199	5,673	315	567
2015	3,799	179	26	570	1,607	95	188	5,358	315	536
2016	3,595	179	26	539	1,513	95	177	5,043	315	504
2017	3,390	179	26	509	1,418	95	166	4,727	315	473
2018	3,186	179	26	478	1,324	95	155	4,412	315	441
2019	2,982	179	26	447	1,229	95	144	4,097	315	410
2020	2,777	179	26	417	1,135	95	133	3,782	315	378
2021	2,573	179	26	386	1,040	95	122	3,467	315	347
2022	2,368	179	26	355	945	95	110	3,152	315	315
2023	2,164	179	26	325	851	95	100	2,836	315	284
2024	1,960	179	26	294	756	95	88	2,521	315	252
2025	1,755	179	26	263	662	95	77	2,206	315	221
2026	1,551	179	26	233	567	95	66	1,891	315	189
2027	1,346	179	26	202	473	95	55	1,576	315	158
2028	1,142	179	26	171	378	95	44	1,261	315	126
2029	938	179	26	141	284	95	33	945	315	95
2030	733	179	26	110	189	95	22	630	315	63
2031	529	179	26	79	95	95	11	315	315	32
end-2031	324	-	-	-	0	-	-	0	-	-

Table A.1: Year-by-year distribution of capital recovery and interests generated during plant operation (ROI) for the favorable case (all costs are rounded and expressed in thousands of escalated euros)

A.1.2 Unfavorable Case

	Common Equity				Preferred Stock			Debt		
Year	BBY	BD	RCEAF	ROI	BBY	BD	ROI	BBY	BD	ROI
2012	9,013	366	54	1,352	3,863	193	452	12,876	644	1,288
2013	8,594	366	54	1,289	3,670	193	429	12,232	644	1,223
2014	8,174	366	54	1,226	3,477	193	407	11,588	644	1,159
2015	7,755	366	54	1,163	3,283	193	384	10,945	644	1,094
2016	7,335	366	54	1,100	3,090	193	362	10,301	644	1,030
2017	6,915	366	54	1,037	2,897	193	339	9,657	644	966
2018	6,496	366	54	974	2,704	193	316	9,013	644	901
2019	6,076	366	54	911	2,511	193	294	8,369	644	837
2020	5,657	366	54	849	2,318	193	271	7,726	644	773
2021	5,237	366	54	786	2,125	193	249	7,082	644	708
2022	4,818	366	54	723	1,931	193	226	6,438	644	644
2023	4,398	366	54	660	1,738	193	203	5,794	644	579
2024	3,979	366	54	597	1,545	193	181	5,150	644	515
2025	3,559	366	54	534	1,352	193	158	4,507	644	451
2026	3,139	366	54	471	1,159	193	136	3,863	644	386
2027	2,720	366	54	408	966	193	113	3,219	644	322
2028	2,300	366	54	345	773	193	90	2,575	644	258
2029	1,881	366	54	282	579	193	68	1,931	644	193
2030	1,461	366	54	219	386	193	45	1,288	644	129
2031	1,042	366	54	156	193	193	23	644	644	64
end-2031	622	-	-	-	0	-	-	0	-	-

Table A.2: Year-by-year distribution of capital recovery and interests generated during plant operation (ROI) for the unfavorable case (all costs are rounded and expressed in thousands of escalated euros)

A.2 Total Required Revenue (TCR)

A.2.1 Favorable Case

Year	TCR	ROI_{ce}	ROI_{ps}	ROI_{d}	OAM	FC	TRR_{cu}	TRR_{ct}
2012	614	662	221	630	2,032	125	4,285	3,825
2013	614	631	210	599	2,066	127	4,248	3,386
2014	614	601	199	567	2,101	130	4,211	2,997
2015	614	570	188	536	2,136	132	4,175	2,653
2016	614	539	177	504	2,172	134	4,140	2,349
2017	614	509	166	473	2,208	136	4,106	2,080
2018	614	478	155	441	2,245	138	4,072	1,841
2019	614	447	144	410	2,283	141	4,039	1,631
2020	614	417	133	378	2,321	143	4,006	1,444
2021	614	386	122	347	2,360	146	3,974	1,279
2022	614	355	111	315	2,400	148	3,943	1,133
2023	614	325	100	284	2,440	150	3,913	1,004
2024	614	294	88	252	2,481	153	3,883	889
2025	614	263	77	221	2,523	156	3,854	788
2026	614	233	66	189	2,566	158	3,826	699
2027	614	202	55	158	2,609	161	3,798	619
2028	614	171	44	126	2,652	164	3,772	549
2029	614	141	33	95	2,697	166	3,746	487
2030	614	110	22	63	2,742	169	3,721	432
2031	614	79	11	32	2,788	172	3,696	383

Table A.3: Year-by-year revenue requirement analyisis for the favorable case (all costs are rounded and expressed in thousands of escalated euros)

A.2.2 Unfavorable Case

Year	TCR	ROI_{ce}	ROI_{ps}	ROI_{d}	OAM	FC	TRR_{cu}	TRR_{ct}
2012	1,257	1,352	452	1,288	2,032	125	6,505	5,808
2013	1,257	1,289	429	1,223	2,066	127	6,391	5,158
2014	1,257	1,226	407	1,159	2,101	130	6,278	4,522
2015	1,257	1,163	384	1,094	2,136	132	6,166	3,963
2016	1,257	1,100	362	1,030	2,172	134	6,054	3,472
2017	1,257	1,037	339	966	2,208	136	5,943	3,042
2018	1,257	974	316	901	2,245	138	5,832	2,664
2019	1,257	911	294	837	2,283	141	5,723	2,332
2020	1,257	849	271	773	2,321	143	5,613	2,042
2021	1,257	786	249	708	2,360	146	5,505	1,787
2022	1,257	723	226	644	2,400	148	5,397	1,563
2023	1,257	660	203	579	2,440	150	5,290	1,367
2024	1,257	597	181	515	2,481	153	5,184	1,195
2025	1,257	534	158	451	2,523	156	5,078	1,044
2026	1,257	471	136	386	2,566	158	4,973	913
2027	1,257	408	113	322	2,609	161	4,869	797
2028	1,257	345	90	258	2,652	164	4,765	696
2029	1,257	282	68	193	2,697	166	4,663	608
2030	1,257	219	45	129	2,742	169	4,561	530
2031	1,257	156	23	64	2,788	172	4,460	462

Table A.4: Year-by-year revenue requirement analyisis for the unfavorable case (all costs are rounded and expressed in thousands of escalated euros)

Appendix B

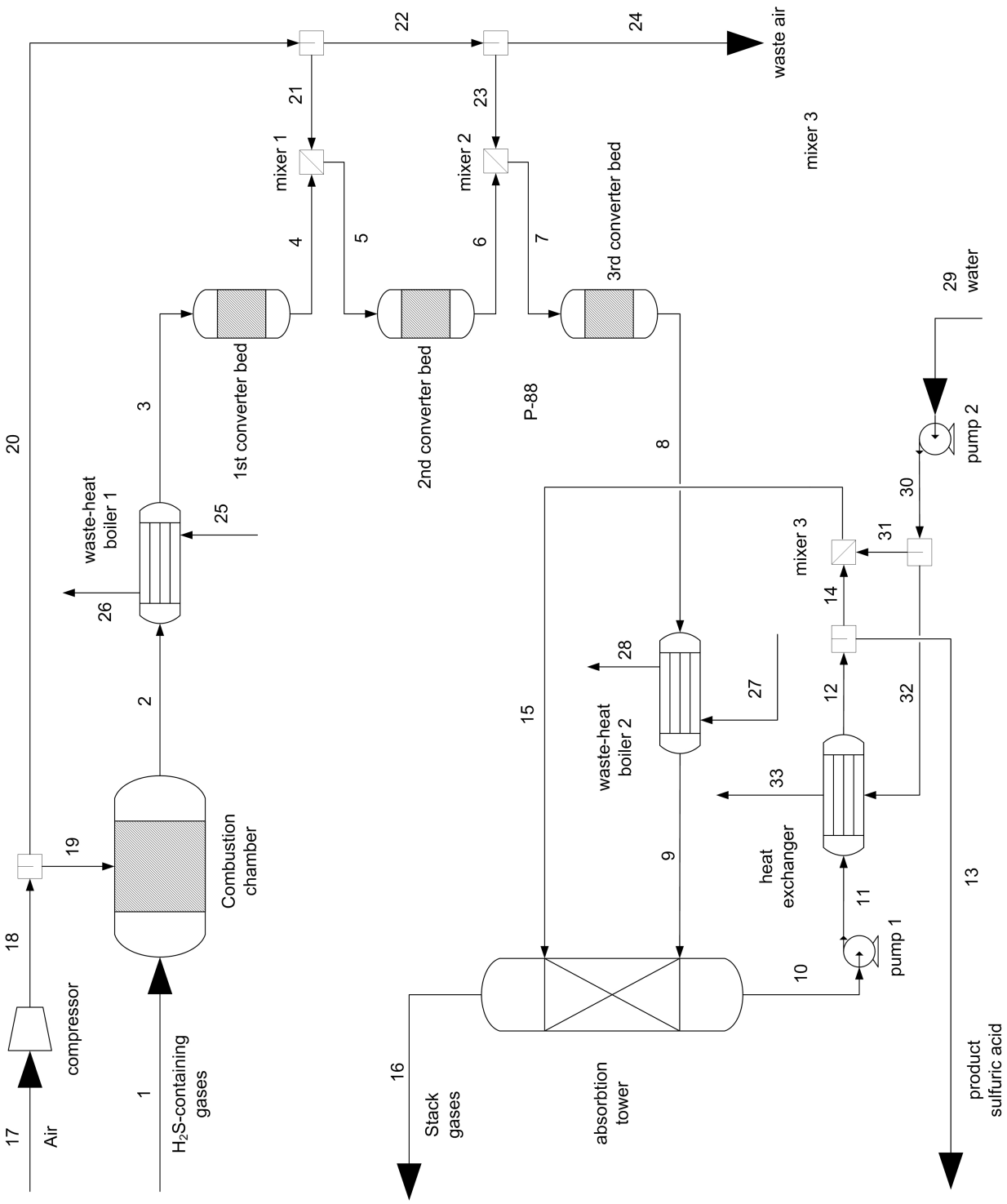


Figure B.1: Reference plant with high anticorrosive heat exchanger (glass heat exchanger)

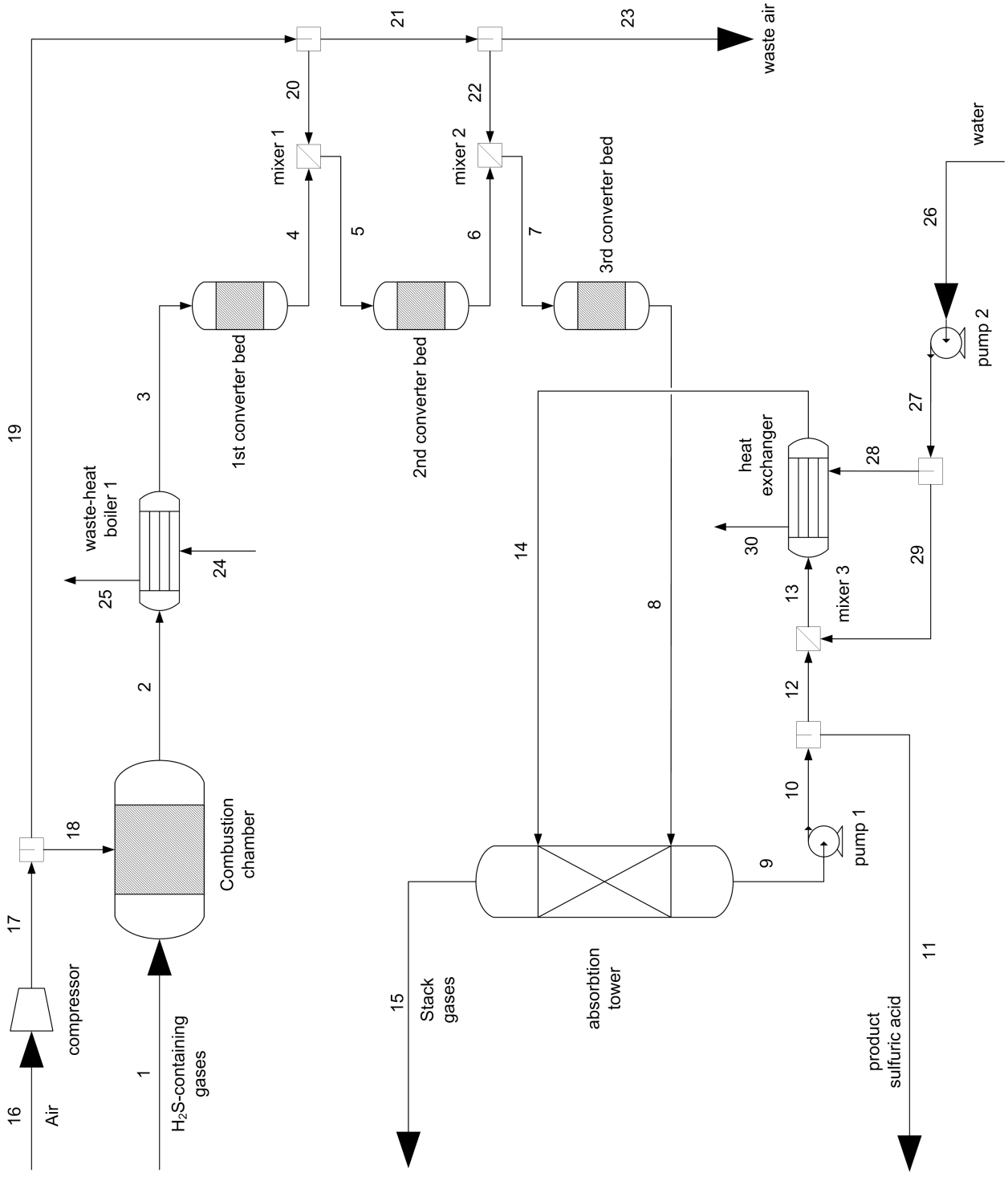


Figure B.2: Improvement II plant design

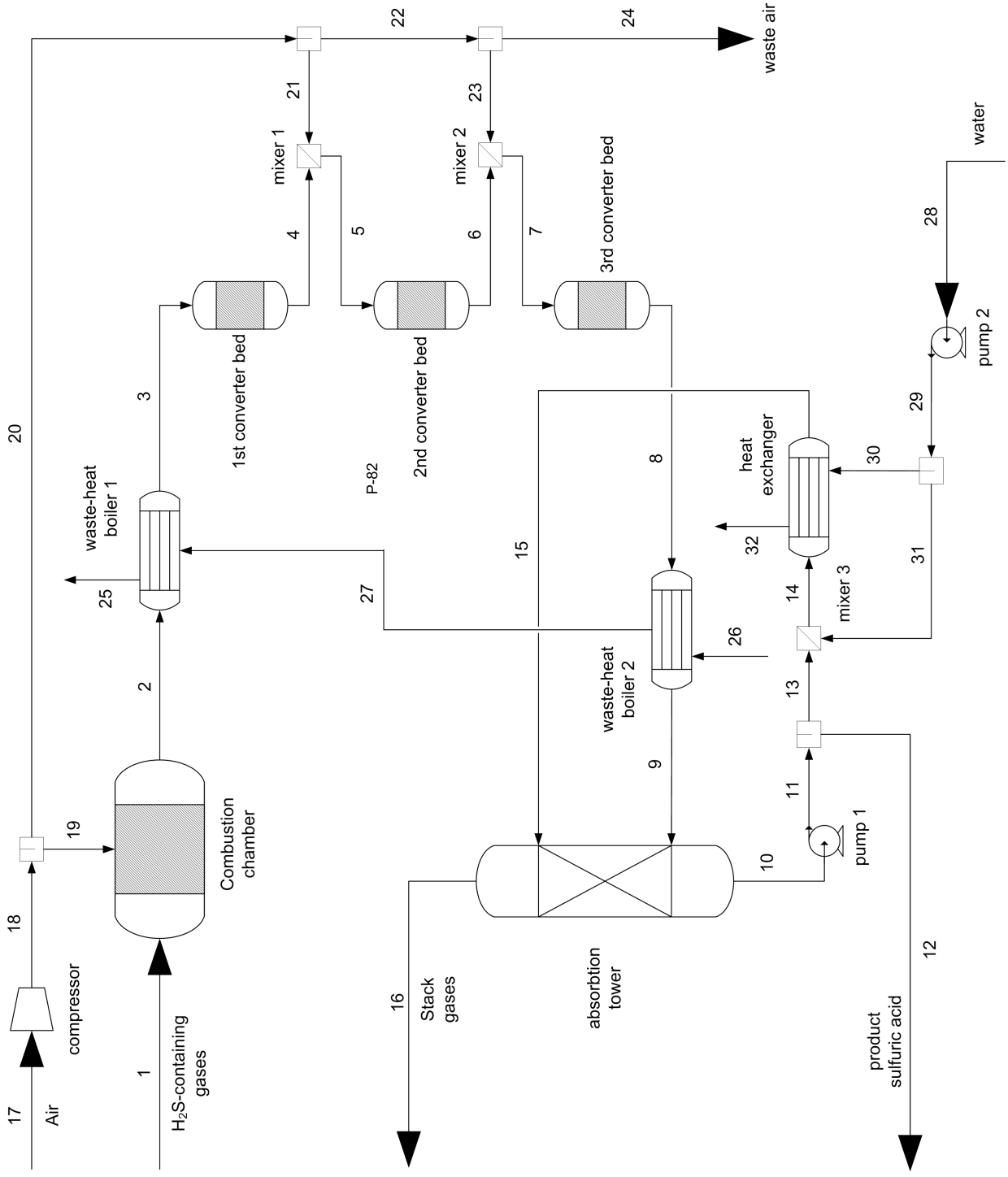


Figure B.3: Improvement III plant design

	Stream n°	$\dot{E}_{tot}$ **[MW]**	**c [euro/GJ]**	**c [ct./kWh]**	$\dot{C}$ **[euro/h]**
Sour gas	1	5.94	0.000	0.000	0.00
SO_2 from c. chamber	2	4.43	4.126	1.485	65.8
SO_2 from boiler	3	2.43	16.52	5.946	145
SO_3 from horde 1	4	2.41	17.07	6.146	148
SO_3 from quench 1	5	2.24	19.82	7.134	159
SO_3 from horde 2	6	2.16	31.78	11.44	247
SO_3 from quench 2	7	2.10	33.22	11.96	251
SO_3 from horde 3	8	2.09	34.55	12.44	260
SO_3 from boiler	9	1.62	55.51	19.98	323
H_2SO_4 from absorbtion	10	51.8	191.1	68.80	35,619
H_2SO_4 from pump	11	51.8	191.1	68.80	35,619
H_2SO_4 to sell	12	0.66	191.1	68.80	454
H_2SO_4 to recirculate	13	51.1	191.1	68.80	35,165
H_2SO_4 mixed with water	14	51.1	191.2	68.82	35,165
H_2SO_4 from heat-exchanger	15	50.8	192.5	69.31	35,182
Stack gas	16	0.04	0.000	0.000	0.00

Table B.1: Thermoeconomic results for the Improvement I: main stream (Intermediate case)

	Stream nº	$\dot{E}_{tot}$ **[MW]**	**c [euro/GJ]**	**c [ct./kWh]**	$\dot{C}$ **[euro/h]**
Atmospheric air	17	0.00	0.000	0.000	0.00
Air from compressor	18	0.08	104.1	37.48	31.5
Air to combustion	19	0.04	104.1	37.48	16.0
Air	20	0.04	104.1	37.48	15.5
Air to quench 1	21	0.03	104.1	37.48	11.29
Air	22	0.01	104.1	37.48	4.26
Air to quench 2	23	0.01	104.1	37.48	4.26
Air released	24	0.00	0.000	0.000	0.00
Water to boiler 1	25	0.04	0.000	0.000	0.00
Vapor from boiler 1	26	1.16	6.333	2.280	26.5
Water to boiler 2	27	0.02	0.000	0.000	0.00
Vapor from boiler 2	28	0.31	21.00	7.56	23.6
Water to pump	29	0.52	0.000	0.000	0.00
Water from pump	30	0.52	0.185	0.066	0.34
Water to heat exchanger	31	0.52	0.185	0.066	0.34
Water to mixer	32	0.00	0.185	0.066	0.00
Water from heat exchanger	33	0.518	0.185	0.066	0.34

Table B.2: Thermoeconomic results for the Improvement I: atmospheric air and water (Intermediate case)

	Stream n°	$\dot{E}_{tot}$ **[MW]**	**c [euro/GJ]**	**c [ct./kWh]**	$\dot{C}$ **[euro/h]**
Sour gas	1	5.94	0.000	0.000	0.00
SO_2 from c. chamber	2	4.43	4.46	1.607	71.2
SO_2 from boiler	3	2.22	21.35	7.685	171
SO_3 from horde 1	4	2.18	22.23	8.005	174
SO_3 from quench 1	5	2.07	24.47	8.811	182
SO_3 from horde 2	6	2.03	37.98	13.67	277
SO_3 from quench 2	7	1.99	38.99	14.04	280
SO_3 from horde 3	8	1.99	40.44	14.56	289
H_2SO_4 from absorbtion	9	53.0	184.16	66.30	35,161
H_2SO_4 from pump	10	53.0	184.16	66.30	35,161
H_2SO_4 to sell	11	0.66	184.16	66.30	437
H_2SO_4 to recirculate	12	52.4	184.16	66.30	34,724
H_2SO_4 mixed with water	13	52.3	184.27	66.34	34,724
H_2SO_4 from heat-exchanger	14	52.0	185.79	66.88	34,750
Stack gas	15	0.04	0.000	0.000	0.00

Table B.3: Thermoeconomic results for the Improvement II: main stream (Intermediate case)

	Stream n°	$\dot{E}_{tot}$ **[MW]**	**c [euro/GJ]**	**c [ct./kWh]**	$\dot{C}$ **[euro/h]**
Atmospheric air	16	0.00	0.000	0.000	0.00
Air from compressor	17	0.07	113.22	40.76	28.1
Air to combustion	18	0.04	113.22	40.76	17.3
Air	19	0.03	113.22	40.76	10.7
Air to quench 1	20	0.02	113.22	40.76	7.97
Air	21	0.01	113.22	40.76	2.73
Air to quench 2	22	0.01	113.22	40.76	2.73
Air released	23	0.00	0.000	0.000	0.00
Water to boiler 1	24	0.05	0.000	0.000	0.00
Vapor from boiler 1	25	1.32	7.21	2.597	34.2
Water to pump	26	0.63	0.000	0.000	0.00
Water from pump	27	0.63	0.19	0.067	0.42
Water to heat exchanger	28	0.63	0.19	0.067	0.42
Water to mixer	29	0.00	0.19	0.067	0.00
Water from heat exchanger	30	0.63	0.19	0.067	0.42

Table B.4: Thermoeconomic results for the Improvement II: atmospheric air and water (Intermediate case)

	Stream n°	$\dot{E}_{tot}$ **[MW]**	**c [euro/GJ]**	**c [ct./kWh]**	$\dot{C}$ **[euro/h]**
Sour gas	1	5.94	0.000	0.000	0.00
SO_2 from c. chamber	2	4.43	4.16	1.498	66.4
SO_2 from boiler	3	2.22	21.61	7.779	173
SO_3 from horde 1	4	2.18	22.46	8.087	176
SO_3 from quench 1	5	2.07	24.68	8.884	184
SO_3 from horde 2	6	2.03	37.17	13.38	271
SO_3 from quench 2	7	1.99	38.15	13.73	274
SO_3 from horde 3	8	1.99	39.48	14.21	283
SO_3 from boiler	9	1.49	60.05	21.62	321
H_2SO_4 from absorbtion	10	45.1	188	67.82	30,601
H_2SO_4 from pump	11	45.1	188	67.82	30,601
H_2SO_4 to sell	12	0.66	188	67.82	447
H_2SO_4 to recirculate	13	44.5	188	67.82	30,154
H_2SO_4 mixed with water	14	44.4	189	67.86	30,154
H_2SO_4 from heat-exchanger	15	44.2	190	68.31	30,167
Stack gas	16	0.04	0.000	0.000	0.00

Table B.5: Thermoeconomic results for the Improvement III: main stream (Intermediate case)

	Stream n°	$\dot{E}_{tot}$ **[MW]**	**c [euro/GJ]**	**c [ct./kWh]**	$\dot{C}$ **[euro/h]**
Atmospheric air	17	0.00	0.000	0.000	0.00
Air from compressor	18	0.07	109	39.37	27.1
Air to combustion	19	0.04	109	39.37	16.8
Air	20	0.03	109	39.37	10.3
Air to quench 1	21	0.02	109	39.37	7.70
Air	22	0.01	109	39.37	2.63
Air to quench 2	23	0.01	109	39.37	2.63
Air released	24	0.00	0.000	0.000	0.00
Vapor from boiler 1	25	1.78	8.61	3.098	55.2
Water to boiler 2	26	0.06	0.000	0.000	0.00
Vapor from boiler 2	27	0.39	10.75	3.869	15.1
Water to pump	28	0.41	0.000	0.000	0.00
Water from pump	29	0.41	0.18	0.066	0.27
Water to heat exchanger	30	0.41	0.18	0.066	0.27
Water to mixer	31	0.00	0.18	0.066	0.00
Water from heat exchanger	32	0.41	0.18	0.066	0.27

Table B.6: Thermoeconomic results for the Improvement III: atmospheric air and water (Intermediate case)

	Stream nº	$\dot{E}_{tot}$ **[MW]**	**c [euro/GJ]**	**c [ct./kWh]**	$\dot{C}$ **[euro/h]**
Compressor	34	0.120	44.69	16.09	19.4
Pump 1	35	0.000	44.69	16.09	0.05
Pump 2	36	0.002	44.69	16.09	0.34

Table B.7: Costs associated with compressor and pumps power for the Improvement I (Intermediate case)

	Stream nº	$\dot{E}_{tot}$ **[MW]**	**c [euro/GJ]**	**c [ct./kWh]**	$\dot{C}$ **[euro/h]**
Compressor	31	0.10	44.69	16.09	15.9
Pump 1	32	0.00	44.69	16.09	0.05
Pump 2	33	0.00	44.69	16.09	0.42

Table B.8: Costs associated with compressor and pumps power for the Improvement II (Intermediate case)

	Stream nº	$\dot{E}_{tot}$ **[MW]**	**c [euro/GJ]**	**c [ct./kWh]**	$\dot{C}$ **[euro/h]**
Compressor	33	0.099	44.69	16.09	15.9
Pump 1	34	0.000	44.69	16.09	0.04
Pump 2	35	0.002	44.69	16.09	0.27

Table B.9: Costs associated with compressor and pumps power for the Improvement III (Intermediate case)

Economic analysis	**[MWh/year]**	**[ct./kWh]**	**[euros/year]**	**[kg/h]**	**[ct./kg]**	**[euros/year]**
Sulfuric acid	5,776	39.8	2.301,759	2,580	10.2	2.301,759
Steam (40 bar)	10,175	16.4	1.665,828	4,134	4.60	1.665,828
Steam (5 bar)	2,737	16.4	448,101	1,506	3.40	448,101
Total			4.415,688			4.415,688

Thermoeconomic analysis	**[MWh/year]**	**[ct./kWh]**	**[euros/year]**	**[kg/h]**	**[ct./kg]**	**[euros/year]**
Sulfuric acid	5,776	68.9	3.977,030	2,580	17.6	3.977,030
Steam (40 bar)	10,175	2.28	231,974	4,134	0.64	231,974
Steam (5 bar)	2,737	7.56	206,924	1,506	1.57	206,924
Total			4.415,929			4.415,929

Table B.10: Rounded average costs per unit of exergy of the plant products calculated through an economic and a thermoeconomic analysis for the Improvement I (Intermediate case)

Economic analyisis	**[MWh/year]**	**[ct./kWh]**	**[euros/year]**	**[kg/h]**	**[ct./kg]**	**[euros/year]**
Sulfuric acid	5,780	38.9	2.248,546	2,581	9.95	2.248,546
Steam (40 bar)	11,524	16.4	1.886,797	4,682	4.60	1.886,797
Total			4.135,343			4.135,343

Thermoeconomic analyisis	**[MWh/year]**	**[ct./kWh]**	**[euros/year]**	**[kg/h]**	**[ct./kg]**	**[euros/year]**
Sulfuric acid	5,780	66.4	3.835,661	2,581	16.97	3.835,661
Steam (40 bar)	11,524	2.60	299,329	4,682	0.73	299,329
Total			4.134,990			4.134,990

Table B.11: Rounded average costs per unit of exergy of the plant products calculated through an economic and a thermoeconomic analysis for the Improvement II (Intermediate case)

Economic analyisis	**[MWh/year]**	**[ct./kWh]**	**[euros/year]**	**[kg/h]**	**[ct./kg]**	**[euros/year]**
Sulfuric acid	5,776	31.97	1.846,622	2,580	8.17	1.846,622
Steam (40 bar)	15,612	16.37	2,556.156	6,343	4.60	2,556.156
Total			4.402,778			4.402,778

Thermoeconomic analyisis	**[MWh/year]**	**[ct./kWh]**	**[euros/year]**	**[kg/h]**	**[ct./kg]**	**[euros/year]**
Sulfuric acid	5,776	67.9	3.919,138	2,580	17.34	3.919,138
Steam (40 bar)	15,612	3.10	483,986	6,343	0.87	483,986
Total			4.403,123			4.403,123

Table B.12: Rounded average costs per unit of exergy of the plant products calculated through an economic and a thermoeconomic analysis Improvement III (Intermediate case)

Thermoeconomic	**Favorable**	**Intermediate**	**Unfavorable**
H_2SO_4	14.9	17.0	20.1
Steam (40 bar)	0.64	0.73	0.87
Economic	**Favorable**	**Intermediate**	**Unfavorable**
H_2SO_4	7.69	9.95	13.3
Steam (40 bar)	4.60	4.60	4.60

Table B.13: Product prices of both thermoeconomic and economic analysis for the Improvement II

Thermoeconomic	**Favorable**	**Intermediate**	**Unfavorable**
H_2SO_4	15.0	17.3	20.8
Steam (40 bar)	0.75	0.87	1.05
Economic	**Favorable**	**Intermediate**	**Unfavorable**
H_2SO_4	5.56	8.17	12.1
Steam (40 bar)	4.60	4.60	4.60

Table B.14: Product prices of both thermoeconomic and economic analysis for the Improvement III

Appendix C

C.1 AD_12_FOR.FOR

```
SUBROUTINE AD12_FOR
INCLUDE 'COMM_BX_AD12.h'
EXTERNAL EXTERNALENTROPIE
EXTERNAL EXTERNALCHEMEXERGY
EXTERNAL COEF_ACTIV

DOUBLE PRECISION t0_2x,p0_2x,hin,sindoub,bb,cc,dd,s0doub
DOUBLE PRECISION tot_liq,xAcid,xWater,eph,gibbsE,etot,gamma(200)
REAL n(200),x(200),tin,pin,aa(200),aux,SV,SL,sin,tin0,pin0,ee(200)
REAL gg(200),hh,ii,jj,kk,ll,mm,nn,oo,h0,vapor0(200),liq0(200)
REAL vaptot0,s0,vapor(200),liq(200),vaptot,ech
INTEGER model

xAcid=0
xWater=0
t0_2x=USPEC(2)
p0_2x=1.01325
n=FC(:,1)/2.20462/3600.0
x=FC(:,1)/sum(FC(:,1))
tin=ft(1)/1.8
pin=fp(1)*0.0689476
USPEC(8)=tin
USPEC(9)=pin
model=USPEC(20)
n=n*2.20462*3600
```

```
t0_2x=t0_2x*1.8
tin=tin*1.8
p0_2x=p0_2x/0.0689476
pin=pin/0.0689476
aa=n
aux=0.0

DO 200 i=1,200
    if (aa(i)/=0) then
        aux=aux+1.0
    endif
200 CONTINUE

USPEC(19)=aux

if (aux==1.0) then
    hin=fh(1)
    USPEC(17)=fv(1)
    CALL ENTROPY(x,ft(1),fp(1),1.0,SV)
    CALL ENTROPY(x,ft(1),fp(1),0.0,SL)
    sindoub=(fv(1)*SV+(1-fv(1))*SL)*sum(aa)
    bb=hin
    cc=t0_2x
    dd=p0_2x
    CALL tpflash(aa,bb,cc,dd,ee,gg,hh,ii,jj,kk,ll,mm,nn,oo)
    h0=ll
    vapor0=ee
    liq0=gg
    vaptot0=mm
    USPEC(18)=vaptot0
    CALL ENTROPY(x,t0_2x,p0_2x,vaptot0,s0)
    s0doub=s0*sum(aa)
    gamma=1.0
else
    CALL tpflash(aa,fh(1),ft(1),fp(1),ee,gg,hh,ii,jj,kk,ll,mm,nn,oo)
```

```
    hin=ll
    vapor=ee
    liq=gg
    vaptot=mm
    USPEC(17)=vaptot
    CALL EXTERNALENTROPIE(n,tin,pin,vapor,liq,sv,sl,sin)
    sindoub=sin
    cc=t0_2x
    dd=1.01325/0.0689476
    CALL tpflash(aa,fh(1),cc,dd,ee,gg,hh,ii,jj,kk,ll,mm,nn,oo)
    h0=ll
    vapor0=ee
    liq0=gg
    vaptot0=mm
    USPEC(18)=mm
    tot_liq=sum(gg)
    xAcid=gg(7)/tot_liq
    xWater=gg(3)/tot_liq
    tin0=t0_2x
    pin0=1.01325/0.0689476
    CALL EXTERNALENTROPIE(n,tin0,pin0,vapor0,liq0,sv,sl,s0)
    s0doub=s0
endif

USPEC(25)=xAcid
USPEC(24)=xWater
hin=hin/0.947817/3600
h0=h0/0.947817/3600
USPEC(10)=hin
USPEC(11)=h0
sindoub=sindoub/0.947817/3600*1.8
s0doub=s0doub/0.947817/3600*1.8
USPEC(12)=sindoub
USPEC(13)=s0doub
tin0=t0_2x
```

```
tin0=tin0/1.8
eph=(hin-h0)-tin0*(sindoub-s0doub)
USPEC(14)=eph

if (aux>1) then
    if (xAcid/=0 .and. xWater/=0) then
        CALL coef_activ(aa,tin0*1.8,pin0,gibbsE,gamma)
        USPEC(22)=gamma(3)
        USPEC(23)=gamma(7)
    else
        gamma=1.0
    endif
else
    USPEC(22)=0
    USPEC(23)=0
endif

CALL excgibbs(aa,tin,pin,gibbsE)
USPEC(21)=gibbsE/0.947817*2.20462
CALL EXTERNALCHEMEXERGY(model,vapor0,liq0,tin0,gamma,ech)
USPEC(15)=ech
etot=eph+ech
etot=etot/1000
USPEC(16)=etot
n=n/2.20462/3600
USPEC(26)=etot/sum(n)
of=ff
ot=tin
op=pin
ov=fv
oc=fc
oh=fh

END SUBROUTINE AD12_FOR
```

C.2 EXTERNALENTROPIE.FOR

```
INCLUDE 'COMM_BX_AD12.h'

DOUBLE PRECISION TDOUB,PDOUB
REAL FEED(200),XCOMPO_V(200),XCOMPO_L(200)
REAL FTOT,vapor(200),liq(200),SOUT_TOT,T,P
REAL ENTROPY_V,ENTROPY_L,so_v,so_l,ftot_v,ftot_l

TDOUB=T
PDOUB=P
FTOT=SUM(FEED)

DO 200 i=1,200
    if (liq(i)/=0.0 .and. feed(i)==0.0) then
        XCOMPO_L(i)=0.0
    else
        XCOMPO_V(i)=vapor(i)/FTOT
        XCOMPO_L(i)=liq(i)/FTOT
    endif
200 CONTINUE

CALL ENTROPY(XCOMPO_V,TDOUB,PDOUB,1.0,ENTROPY_V)
CALL ENTROPY(XCOMPO_L,TDOUB,PDOUB,0.0,ENTROPY_L)
so_v=ENTROPY_V*ftot
so_l=ENTROPY_L*ftot
SOUT_TOT=(ENTROPY_V+ENTROPY_L)*FTOT

END SUBROUTINE EXTERNALENTROPIE
```

C.3 EXTERNALCHEMEXERGIE.FOR

```
SUBROUTINE EXTERNALCHEMEXERGY(MODE,VAPOR,LIQ,T,coef,EOUT_CHEM)
INCLUDE 'COMM_JS_AD13.H'
EXTERNAL ECH_TAB2FOR
```

```
INTEGER MODE
DOUBLEPRECISION coef(200)
REAL EOUT_CHEM, EOUT_CHEM_V, EOUT_CHEM_L, T, FEED(200)
REAL ech_tab_g, ech_tab_l, vapor(200), liq(200), ftotvap, ftotliq
REAL xvapor(200), xliq(200)

EOUT_CHEM_V=0.0
EOUT_CHEM_L=0.0
ftotvap=sum(vapor)
ftotliq=sum(liq)
feed=vapor+liq

DO 200 i=1,200
    if (feed(i)/=0) then
        CALL ECH_TAB2FOR(MODE,IDCOM(i),ech_tab_g,ech_tab_l)
            if (vapor(i)/=0.0 .and. liq(i)/=0.0) then
                xvapor(i)=vapor(i)/ftotvap
                xliq(i)=liq(i)/ftotliq
                EOUT_CHEM_V=EOUT_CHEM_V+xvapor(i)*ech_tab_g+
                * 8.314*T*xvapor(i)*log(xvapor(i))
                EOUT_CHEM_L=EOUT_CHEM_L+xliq(i)*ech_tab_l+
                * 8.314*T*xliq(i)*log(coef(i)*xliq(i))
            else if (vapor(i)/=0.0 .and. liq(i)==0.0) then
                xvapor(i)=vapor(i)/ftotvap
                EOUT_CHEM_V=EOUT_CHEM_V+xvapor(i)*ech_tab_g+
                * 8.314*T*xvapor(i)*log(xvapor(i))
            else if (vapor(i)==0.0 .and. liq(i)/=0.0) then
                xliq(i)=liq(i)/ftotliq
                EOUT_CHEM_L=EOUT_CHEM_L+xliq(i)*ech_tab_l+
                * 8.314*T*xliq(i)*log(coef(i)*xliq(i))
            endif
    endif
200 CONTINUE

EOUT_CHEM_V=EOUT_CHEM_V*ftotvap/2.20462/3600.0
```

```
EOUT_CHEM_L=EOUT_CHEM_L*ftotliq/2.20462/3600.0
EOUT_CHEM=EOUT_CHEM_V+EOUT_CHEM_L

END SUBROUTINE EXTERNALCHEMEXERGY
```

C.4 ECH_TAB2FOR.FOR

```
SUBROUTINE ECH_TAB2FOR(MODES,IDCOM,EOUT_TAB_G,EOUT_TAB_L)
INCLUDE 'bxa.h'

INTEGER IDCOM, idtab, MODES
REAL eout_tab_g, eout_tab_l

open (9, FILE='datai_g.dat', STATUS='OLD')
open (10, FILE='datai_l.dat', STATUS='OLD')
open (11, FILE='datai_g2.dat', STATUS='OLD')
open (12, FILE='datai_l2.dat', STATUS='OLD')

if (MODES==0) then
    read (9,230) idtab, eout_tab_g
    read (10,230) idtab, eout_tab_l
    DO 200 i=1,200
        if (IDCOM==idtab) then
            goto 3000
        else
            read (9,230) idtab, eout_tab_g
            read (10,230) idtab, eout_tab_l
        end if
    200 CONTINUE
else
    read (11,230) idtab, eout_tab_g
    read (12,230) idtab, eout_tab_l
    DO 300 i=1,200
        if (IDCOM==idtab) then
            goto 3000
```

```
        else
            read (11,230) idtab, eout_tab_g
            read (12,230) idtab, eout_tab_l
        end if
    300 CONTINUE
endif

230 FORMAT (I4,1x,F10.0)
3000 close (9)
close (10)
close (11)
close (12)

END SUBROUTINE ECH_TAB2FOR
```

C.5 COEF_ACTIV.FOR

```
SUBROUTINE COEF_ACTIV(feed,T,P,gibbs_ex,coef)
INCLUDE 'COMM_BX_AD12.h'
EXTERNAL EXTERNALENTROPIE
EXTERNAL EXCGIBBS

DOUBLE PRECISION gibbs_exc,deriv(200),coef(200),TDOUB,PDOUB
DOUBLE PRECISION gibbs_ex,bb,cc,dd,ftot_l,xH2SO4,xH2O,dx
DOUBLE PRECISION derivada,gEaprox
REAL T,P,Rconst,xvect(39),yvect(39),escal,stream(200)
REAL bvect1(7),sspoly(7),stat(10),feed(200),aa(200),ee(200)
REAL gg(200),hh,ii,jj,kk,ll,mm,nn,oo,bvect2(7)
INTEGER nobs,ndeg

gibbs_exc=0.0
deriv=0.0
coef=0.0
TDOUB=T
PDOUB=P
```

```
Rconst=8.314*0.947817/(1.8*2.20462)
coef=1.0
nobs=39
ndeg=6
xvect=0.0
yvect=0.0
escal=0.0
stream=0.0

DO 200 i=1,nobs
    escal=escal+0.025
    xvect(i)=escal
200 CONTINUE

escal=0.0

DO 300 i=1,nobs
    escal=escal+0.025
    stream(3)=(1-escal)
    stream(7)=escal
    CALL excgibbs(stream,T,P,gibbs_ex)
    yvect(i)=gibbs_ex
300 CONTINUE

yvect=yvect/(Rconst*T)
CALL RCURV(nobs,xvect,yvect,ndeg,bvect1,sspoly,stat)
aa=feed
bb=1.0
cc=TDOUB
dd=PDOUB
CALL tpflash(aa,bb,cc,dd,ee,gg,hh,ii,jj,kk,ll,mm,nn,oo)
ftot_l=sum(gg)
xH2SO4=gg(7)/ftot_l
xH2O=gg(3)/ftot_l
dx=0.00001
```

```
derivada=0.0
gEaprox=bvect1(1)

DO 400 i=1,6
    derivada=derivada+bvect1(i+1)*((xH2SO4+dx)**i-xH2SO4**i)
    gEaprox=gEaprox+bvect1(i+1)*xH2SO4**i
400 CONTINUE

derivada=derivada/dx
coef(3)=gEaprox-xH2SO4*derivada
coef(3)=exp(coef(3))
nobs=39
ndeg=6
escal=0.0
stream=0.0
xvect=1-xvect
CALL RCURV(nobs,xvect,yvect,ndeg,bvect2,sspoly,stat)
derivada=0.0
gEaprox=bvect2(1)

DO 500 i=1,6
    derivada=derivada+bvect2(i+1)*((xH2O+dx)**i-xH2O**i)
    gEaprox=gEaprox+bvect2(i+1)*xH2O**i
500 CONTINUE

derivada=derivada/dx
coef(7)=gEaprox-xH2O*derivada
coef(7)=exp(coef(7))

END SUBROUTINE COEF_ACTIV
```

C.6 COEF_ACTIV.FOR

```
SUBROUTINE EXCGIBBS(feed,T,P,gibbs_exc)
INCLUDE 'COMM_BX_AD12.h'
```

```
EXTERNAL EXTERNALENTROPIE

DOUBLE PRECISION gibbs,gibbs_zero,gibbs_exc,TDOUB,PDOUB,bb,cc,dd
DOUBLE PRECISION enthalpy_l,entropy_l
REAL T,P,Rconst,feed(200),aa(200),ee(200),gg(200),hh,ii,jj,kk,ll
REAL mm,nnoo,feed_l(200),ftot,ftot_l,s_v,s_l,stot,unit(200)
REAL xcomp_l,h_i_zero,s_i_zero

gibbs=0.0
gibbs_zero=0.0
gibbs_exc=0.0
TDOUB=T
PDOUB=P
Rconst=8.314*0.947817/(1.8*2.20462)
aa=feed
bb=1.0
cc=TDOUB
dd=PDOUB
CALL tpflash(aa,bb,cc,dd,ee,gg,hh,ii,jj,kk,ll,mm,nn,oo)
enthalpy_l=kk
feed_l=gg
ftot=sum(feed)
ftot_l=sum(feed_l)
CALL EXTERNALENTROPIE(feed,T,P,ee,gg,s_v,s_l,stot)
entropy_l=s_l
gibbs=(enthalpy_l-T*entropy_l)/ftot_l

DO 200 i=1,200
    if (feed_l(i)/=0.0 .and. feed(i)/=0.0) then
        unit=0.0
        unit(i)=feed_l(i)
        xcomp_l=feed_l(i)/ftot_l
        aa=unit
        bb=1.0
        CALL tpflash(aa,bb,cc,dd,ee,gg,hh,ii,jj,kk,ll,mm,nn,oo)
```

```
        h_i_zero=ll
        unit=0.0
        unit(i)=feed_l(i)
        CALL EXTERNALENTROPIE(unit,T,P,ee,gg,s_v,s_l,s_i_zero)
        gibbs_zero=(h_i_zero-T*s_i_zero)/feed_l(i)*xcomp_l
        gibbs_exc=gibbs_exc-gibbs_zero-Rconst*T*xcomp_l*
        * log(xcomp_l)
    end if
200 CONTINUE

gibbs_exc=gibbs_exc+gibbs

END SUBROUTINE EXCGIBBS
```